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Infra-Red and Raman Spectra of Polyatomic Molecules

IX. Dimethyl Acetylene, C_4H_6*

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The infra-red absorption of gaseous C_4H_6 has been measured from 2 to 24μ, and the Raman spectrum of the liquid studied. Analysis of the data permits the determination of all the fundamental frequencies of the molecule. The frequencies are fitted closely with a modified valence-force potential function in which the methyl-group force constants are those previously determined for ethane.

THE dimethyl acetylene molecule, like the ethane molecule, contains one degree of freedom which corresponds to the internal rotation of one methyl group relative to the other. In ethane this rotation is hindered by a barrier of about 2750 cal./mole (assuming the cosine form). It is of interest to determine the magnitude of the barrier in dimethyl acetylene; here the methyl groups are quite far removed, so that we may expect this case to give the smallest restricting potential.

The spectroscopic study which is reported here was undertaken in order to obtain the knowledge of the vibrational frequencies of the molecule which is necessary if the magnitude of the restricting potential is to be accurately determined. The results obtained are also of interest in that the normal coordinate calculations are distinctly encouraging to the hope that certain bond force constants can be transferred from one molecule (ethane) to another of similar structure (dimethyl acetylene).

Studies on the heat capacity of the gas are now in progress, and preliminary results indicate that the restricting potential is less than 500 cal./mole.[1]

EXPERIMENTAL

Infra-red absorption

The material used was made available through the generosity of Professor G. B. Kistiakowsky; it was prepared by Dr. J. B. Conn for use in the hydrogenation calorimeter, and its preparation and purity will be described in a future publication of the series on heats of hydrogenation.

The infra-red absorption of the gas was studied from 2 to 24μ; fluorite, rocksalt, and KBr prisms were used in the appropriate spectral regions. The infra-red spectrometer has been previously described.[2] The absorption spectrum is shown in Fig. 1; the frequencies of the minima are tabulated in Table I. The extremely weak shoulder at 1664 cm^{-1} is doubtful. The accuracy

* A preliminary report of this study was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Baltimore, April, 1939.
† National Research Fellow in Chemistry.

[1] B. L. Crawford, Jr., and W. W. Rice, J. Chem. Phys. **7**, 437 (1939).
[2] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197, 247 (1938).

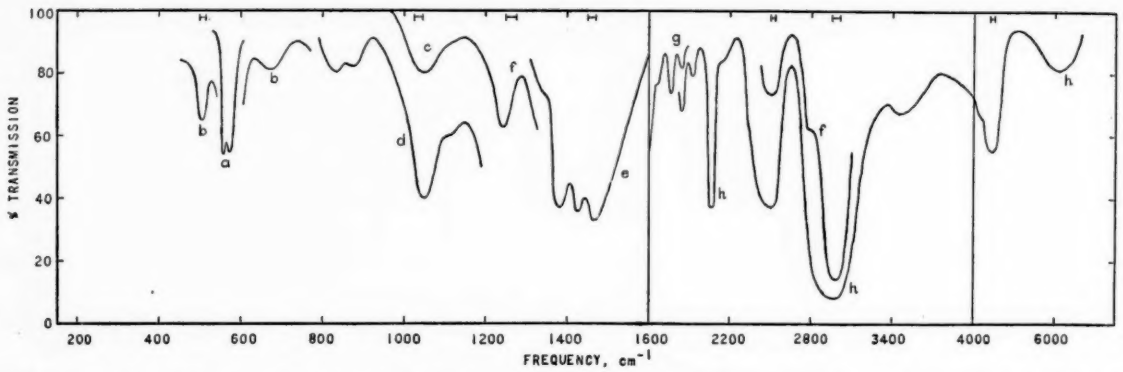

FIG. 1. Infra-red absorption of dimethyl acetylene vapor. Cell length, 30 cm. Pressures : KBr prism: *a*, 100 mm; *b*, 412 mm. NaCl prism: *c*, 103 mm; *d*, 392 mm. CaF_2 prism: *e*, 44 mm; *f*, 98 mm; *g*, 255 mm; *h*, 530 mm. Slit widths are indicated near the top of the plot.

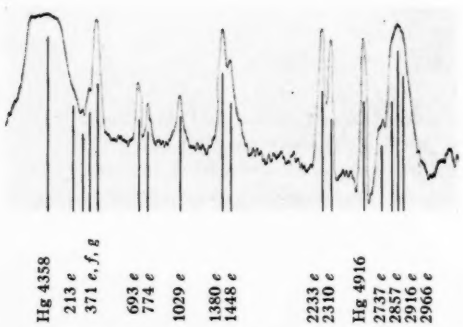

FIG. 2. Microphotometer tracing of the Raman spectrum of liquid dimethyl acetylene, excited by the Hg 4358 triplet. Notation for the exciting lines: *e*, 22938; *f*, 22995; *g*, 23039; *k*, 24705 cm^{-1}.

of the frequency measurements may be estimated from the slit widths shown in Fig. 1.

Raman effect

The Raman effect of the liquid was also studied, using the apparatus previously described.[2] Polarization studies[3] were also made. A microphotometer tracing of the Raman spectrum is shown in Fig. 2; tracings of the polarization plates are shown in Fig. 3. The frequency shifts observed, compared with those found by previous investigators,[4–7] are tabulated in Table II. The 2114 cm^{-1} shift found by Kohlrausch, Pongratz, and Seka, and attributed by them to ethyl acetylene, is omitted from Table II. The intensity estimates are those given by the

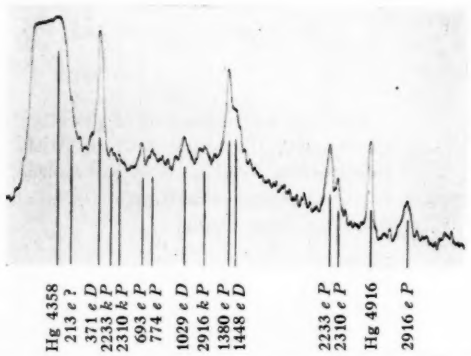

FIG. 3a. Microphotometer tracing of Raman plate taken with the exciting light plane polarized *parallel* to the axis of the Raman tube. Notation for exciting lines as in FIG. 2. *P*, polarized ($\rho < 6/7$); *D*, depolarized ($\rho = 6/7$).

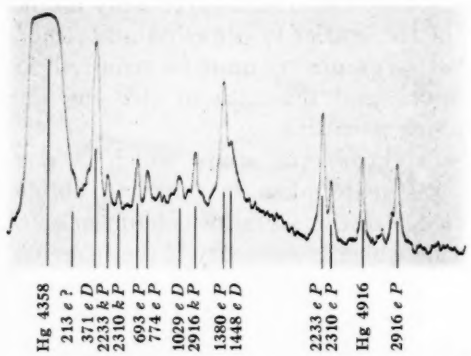

FIG. 3b. Microphotometer tracing of Raman plate taken with the exciting light plane polarized *perpendicular* to the axis of the Raman tube. Notation as in FIG. 3a.

[3] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938).
[4] G. Glockler and H. M. Davis, J. Chem. Phys. **2**, 881 (1934).
[5] G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 408 (1938).
[6] B. Gredy, Comptes rendus **197**, 327 (1933).
[7] K. W. F. Kohlrausch, A. Pongratz and R. Seka, Monatshefte **70**, 213 (1937).

several authors. The agreement is quite satisfactory with regard to the frequencies of the principal lines; the relative intensity estimates, however, differ markedly in some cases.

The Vibration Frequencies

Symmetry

The dimethyl acetylene molecule has the same symmetry as the ethane molecule, and the treatment given by Howard[8] is appropriate. Using his notation for the point group D_{3h}', we have for the structure of the normal coordinate representation

$$\Gamma = 4A_1 + 3\bar{A}_2 + \bar{A}_1 + 4E + 4\bar{E},$$

where the coordinate for the internal rotation

[8] J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

TABLE I. *The infra-red spectrum of dimethyl acetylene, observed and calculated.*

Observed Frequency and Int'y*	Calc'd Freq'y	Assignment and Symmetry	Observed Frequency and Int'y*	Calc'd Freq'y	Assignment and Symmetry
	158	371–213, $\bar{A}_1+\bar{A}_2+\bar{E}$	1763 *W*	1775	1050+725, E
	213	Fund., E		1819	1448+371, A_1+A_2+E
	426	213^2, A_1+E		1839	1468+371, $\bar{A}_1+\bar{A}_2+\bar{E}$
	481	694−213, E§			
			1842 *MW*	1851	1126+725, $\bar{A}_2$
507 *W*	529	371^2−213, A_1+A_2+2E	1920 *W*	1948	1380+(568), $\bar{A}_1+\bar{A}_2+\bar{E}$‡
	561	774−213, E§		2058	1029^2, A_1+E
561, 575 } *S*†	584	213+371, $\bar{A}_1+\bar{A}_2+\bar{E}$		2057	2270−213, E
			2066 *MS*	2079	1029+1050, $\bar{A}_1+\bar{A}_2+\bar{E}$
	658	1029−371, A_1+A_2+E		2100	1050^2, A_1+E
671 *VW*	679	1050−371, $\bar{A}_1+\bar{A}_2+\bar{E}$			
—	742	371^2, A_1+E§		2105	1380+725, $\bar{A}_2$
			2140 *W*	2155	1029+1126, E
—	755	1126−371, E		2193	1468+725, E
	816	1029−213, $\bar{A}_1+\bar{A}_2+\bar{E}$			
835 *W*	837	1050−213, A_1+A_2+E		2409	1029+1380, E
				2430	1050+1380, E
877 *W*	880	1448−(568), A_1+A_2+3E‡		2477	1448+1029, A_1+A_2+E
—	938	725+213, E			
—	1009	1380−371, E		2483	2270+213, E
				2497	1468+1029, $\bar{A}_1+\bar{A}_2+\bar{E}$
1050 *M*	1050	Fund., E		2498	1050+1448, $\bar{A}_1+\bar{A}_2+\bar{E}$
	1077	1448−371, A_1+A_2+E	2500 *MS*	2506	1380+1126, $\bar{A}_2$
	1097	1468−371, $\bar{A}_1+\bar{A}_2+\bar{E}$		2518	1468+1050, A_1+A_2+E
				2574	1448+1126, E
1126 *W*	1126	Fund., $\bar{A}_2$			
	1167	1380−213, E		2595	2966−371, A_1+A_2+E
	1235	1448−213, $\bar{A}_1+\bar{A}_2+\bar{E}$		2605	2976−371, $\bar{A}_1+\bar{A}_2+\bar{E}$
				2703	2916−213, E
1240 *M*	1242	1029+213, $\bar{A}_1+\bar{A}_2+\bar{E}$			
	1255	1468−213, A_1+A_2+E		2753	2966−213, $\bar{A}_1+\bar{A}_2+\bar{E}$
	1263	1050+213, A_1+A_2+E		2760	1380+1380, $\bar{A}_2$
			2785 *W*	2763	2976−213, A_1+A_2+E
1340 *W*	1337	1029+1050−371^2, $2\bar{A}_1+2\bar{A}_2+4\bar{E}$			
1380 *M*	1380	Fund., $\bar{A}_2$		2828	1448+1380, E
	1400	1029+371, A_1+A_2+E		2848	1468+1380, E
				2896	1448+1448, A_1+A_2+E
1425 *MW*	1421	1050+371, $\bar{A}_1+\bar{A}_2+\bar{E}$			
1468 *S*	1468	Fund., E		2916	1448+1468, $\bar{A}_1+\bar{A}_2+\bar{E}$
	1497	1126+371, E		2936	1468+1468, A_1+A_2+E
—	1593	1380+213, E	2976 *VS*	2976	Fund., E, $\bar{A}_2$
			3450 *MW*		} various combinations
1664 ?	1661	1448+213, $\bar{A}_1+\bar{A}_2+\bar{E}$	4140 *W*		
	1681	1468+213, A_1+A_2+E	4425 *MS*		
	1751	1380+371, E	6100 *MW*		

* *W* = weak; *VW* = very weak; *M* = medium; *S* = strong; *VS* = very strong.
† Resolved doublet; calculated $P-R$ separation, 14.2 cm^{-1}. See text.
‡ 568 is the combination level (213+371), $\bar{A}_1+\bar{A}_2+\bar{E}$.
§ The A_1 component of (371^2) interacts with the A_1 fundamental at 725 to give two levels, both A_1, at 694 and 774.

TABLE II. *The Raman spectrum of dimethyl acetylene. Frequencies in cm^{-1}.*§

GLOCKLER*	GREDY[6]	KOHLRAUSCH†	PRESENT WORK	ASSIGNMENT AND SYMMETRY
——	——	144 (2, ?)	——	$371-213=158$, $\bar{A}_1+\bar{A}_2+\bar{E}$
213 (1, *b*)	212 (*W*, *b*)	209 (2, *b*)	213 (*VW*)	Fund., E
——	351 (*W*)	——	——	——
374 (5, *b*)	375 (*S*)	371 (10)	371 (*VVS*, *D*)	Fund., $\bar{E}$
400 (00)	——	——	——	$(213^2=426, A_1+E)$
——	——	508 (0)	——	$371^2-213=529$, A_1+A_2+2E
687 (3, *b*) / 697.4 (4)	695 (*W*)	692 (3)	693 (*M*, *P*)	Fund., 725, A_1
773.5 (4) / 788.5 (3)	773 (*VW*)	767 (½)	774 (*M*, *P*)	$371^2=742$, A_1+E
——	——	834 (½)	——	$1050-213=837$, A_1+A_2+E
——	971 (*W*)	——	——	——
1029 (3)	——	1025 (0)	1029 (*M*, *D*)	Fund., $\bar{E}$
1243 (0)	——	——	——	$1468-213=1255$, A_1+A_2+E‡
1379 (5, *b*)	1383 (*S*)	1380 (7)	1380 (*S*, *P*)	Fund., A_1
1447 (4, *b*)	1441 (*W*) / 1455 (*W*)	1466 (2, *b*)	1448 (*MS*, *D*)	Fund., $\bar{E}$
2201.40 (1)	——	——	——	C^{13} isotope effect, shifted from
2280.2 (1)	——	——	——	the 2270 doublet.
2234.60 (6)	2238 (*S*)	2233 (8)	2233 (*VS*, *P*)	Fund., 2270, A_1
2312.65 (6)	2316 (*M*)	2311 (5)	2310 (*VS*, *P*)	$1126^2=2252$, A_1
2736.8 (3)	——	2737 (2)	2737 (*MW*)	$1380^2=2760$, A_1‡
2861.8 (4)	2862 (*M*)	2860 (4, *b*)	2857 (*M*)	$1448^2=2896$, A_1+E‡
2920 (7)	2923 (*VS*)	2918 (12, *b*)	2916 (*VS*, *P*)	Fund., A_1
2961 (4, *b*)	2961 (*VW*)	2958 (5, *b*)	2966 (*MW*)	Fund., $\bar{E}$
——	2996	——	——	——

* Glockler and Davis (reference 4) as corrected by Glockler and Renfrew (reference 5).
† Kohlrausch, Pongratz, and Seka, reference 7.
‡ For other possible assignments, see Table I in the appropriate frequency range.
§ Intensities are given in parentheses: *b* = broad, *S* = strong, *M* = medium, *W* = weak, *VW* = very weak, *P* = polarized ($\rho \lesssim 6/7$), *D* = depolarized ($\rho = 6/7$).

(symmetry $\bar{A}_1$) is included, but those for the over-all translations and rotations are omitted. The A vibrations are nondegenerate, the E vibrations doubly degenerate; the unbarred vibrations are symmetrical, the barred vibrations antisymmetrical, to reflection in a plane perpendicular to the figure axis and bisecting the C−C triple bond. (For a rigorous discussion of this symmetry operation, see Howard's paper.[8])

The selection rules are also the same (see Table III). The ambiguity with respect to the Raman activity of the E vibrations arises from the same source as in the ethane case. If the internal rotation is free, the E vibrations will be Raman-active; if the rotation is restricted, they will be active or inactive in the Raman effect according as the equilibrium position corresponds to the D_{3h} (eclipsed) or the D_{3d} (staggered) configuration.

Frequency types

If we consider the various types of "bond frequencies" to be expected in dimethyl acetylene, we may apportion them among the symmetry classes as shown in Table III. (The internal rotation is omitted.) The frequencies to be expected for the several vibrations may be estimated by analogy with other molecules, in particular the methyl halides and ethane for the methyl group frequencies, and acetylene for the triple bond stretching frequency. The C−H and C≡C stretching frequencies need no comment. The ethane assignment recently proposed by Barker[9] would require changes in the expected frequencies for C−H bending; it will appear, however, that the polarization data for dimethyl acetylene leave no doubt as to the correctness

[9] E. F. Barker, J. Chem. Phys. **7**, 277 (1939).

of these values in Table III. The CH_3 rocking frequencies should lie near 1000 cm^{-1}. In ethane, these two frequencies are split apart (827 and 1170 cm^{-1})[10] by the strong interaction between methyl groups; in dimethyl acetylene, the methyl groups being far apart, we should expect these frequencies to lie quite close together.

The C−C stretching frequencies are more uncertain. Despite the shorter C−C bond length in dimethyl acetylene, we may expect these frequencies to lie near 1000 cm^{-1}. The effect of the different masses involved in the two vibrations will split them, however, so that we may expect the symmetrical one (A_1) to lie somewhat below 1000 cm^{-1}, and the unsymmetrical one ($\bar{A}_2$) somewhat above.

The carbon chain bending frequencies may be estimated from the case of methyl acetylene.[11] This molecule has two bending frequencies at 333 and 642 cm^{-1}. The latter may be identified with the bending of the C≡C−H angle, since it lies near the bending frequencies of C_2H_2 (605 and 730 cm^{-1}); the 333 cm^{-1} frequency is then associated with the C≡C−CH_3 angle, and the bending frequencies in dimethyl acetylene should lie near this value.

Assignment

The selection rules (Table III) allow but four polarized Raman lines arising from fundamentals; actually six such lines are found at 693, 774, 1380, 2233, 2310, and 2916 cm^{-1} (Table II). Two cases of accidental degeneracy are indicated: one arising from interaction between a fundamental at about 725 cm^{-1} and the first overtone of the 371 Raman line ($371^2=742$); the other from a fundamental at about 2270 cm^{-1} and the first overtone of a frequency near 1135 cm^{-1}. We thus have determined the A_1 frequencies to be 725, 1380, 2270, and 2916 cm^{-1}, as given in Table IV. It is to be noted that in this case, unlike that of ethane, the 1380 cm^{-1} fundamental appears in the Raman effect.

Comparison of the observed frequencies with the estimates and selection rules of Table III allows us immediately to assign the fundamentals above 1300 cm^{-1} as shown in Table IV. (The 2976 cm^{-1} infra-red band is undoubtedly an unresolved complex containing both the $\bar{A}_2$ and E fundamentals; our resolution in this region is quite low.)

The two carbon-chain bending frequencies may be assigned to the Raman lines at 213 and 371 cm^{-1}; since we should expect the E vibration to be the more weakly Raman-active, we assign this fundamental to the 213 cm^{-1} line. The depolarized Raman line at 1029 cm^{-1}, obviously a fundamental, may be assigned to the $\bar{E}$ CH_3 rocking frequency; thus the assignment of the $\bar{E}$ fundamentals is completed.

The two remaining unassigned fundamentals are the E CH_3 rocking vibration and the $\bar{A}_2$ C−C stretching. One of these must lie near 1135 cm^{-1}, as is shown by the resonance splitting of the 2270 A_1 Raman line, discussed above. The only observed frequency near this value is the 1126 cm^{-1} infra-red band.[12] For the other un-

TABLE III. *Types of vibrations in dimethyl acetylene and their distribution among the symmetry classes.*

TYPE OF VIBRATION	A_1	$\bar{A}_2$	E	$\bar{E}$	EXPECTED FREQUENCY
C−H stretching	1	1	1	1	2900–3000
C≡C stretching	1	0	0	0	2100–2200
C−H bending, ⊥*	0	0	1	1	1440–1480
C−H bending, ∥*	1	1	0	0	1380
CH_3 rocking	0	0	1	1	*ca.* 1000
C−C stretching	1	1	0	0	*ca.* 1000
C−C≡C−C bending	0	0	1	1	*ca.* 300
Totals	4	3	4	4	
Activity†	*R, P*	*I,* ∥	*I,* ⊥ *R, D*?	*R, D*	

* ∥ or ⊥ to the axis of the CH_3 group.
† *R, P* = Raman active, polarized ($\rho \ll 6/7$); *R, D* = Raman active, depolarized ($\rho = 6/7$); *I,* ∥ = infra-red-active, parallel bands; *I,* ⊥ = infra-red-active, perpendicular bands.

[10] B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, J. Chem. Phys. **6**, 682 (1938); and reference 17.
[11] B. L. Crawford, Jr., J. Chem. Phys. **7**, 140 (1939).

[12] It would seem more natural to assign 1126 to the overtone of the 568 cm^{-1} band ($568^2=1136$). However, the 568 cm^{-1} band cannot be a fundamental; it is a parallel-type band and would therefore have to be assigned to the A_2 C−C stretching frequency, which surely lies much higher. If 568 cm^{-1} is a combination tone, 1126 cm^{-1} would have to be a quaternary combination if it were not a fundamental, and since the resonance splitting mentioned above demands a fundamental near 1135 cm^{-1}, the assignment given seems the most satisfactory. The possibility of the resonance splitting arising from a *binary combination* near 2270 cm^{-1}, instead of an overtone, has not been overlooked. Such a combination, however, would have to be of type ($\bar{A}_2 \times \bar{A}_2$), ($E \times E$), or ($\bar{E} \times \bar{E}$), in order to have a component of symmetry A_1. A study of the frequencies will show the impossibility of finding a reasonable assignment which satisfies this condition; we have accordingly assumed an overtone to be responsible for the resonance splitting.

assigned fundamental, we choose the 1050 cm^{-1} infra-red band, partly because of its fairly strong intensity, and partly because combination assignments indicate this frequency (e.g., the 671 and 835 cm^{-1} bands). We assign 1050 to the E, and 1126 to the $\bar{A}_2$ class, thus completing the assignments of fundamentals as given in Table IV.

Using the fundamentals thus assigned, the frequencies of all infra-red-active binary combinations and overtones below 3000 cm^{-1} were calculated; difference tones involving the 213 and 371 cm^{-1} fundamentals were included (the Boltzmann factors at 298°K being 0.35 and 0.17, respectively). These calculated frequencies are compared with the observed spectrum in Table I. Certain ternary and quaternary combinations have been added, to account for all the observed bands.

The doublet structure observed in the 568 cm^{-1} band indicates that this is of the parallel type, in agreement with the selection rules. The observed $P-R$ branch separation of 14 cm^{-1} agrees quantitatively with the value of 14.2 cm^{-1} calculated from Gerhard and Dennison's formula[13] (interatomic distances used in finding the moments of inertia were those given below); the nonappearance of the Q branch also agrees with their treatment.

Since combination tones appear more weakly in the Raman effect than in infra-red absorption, the complete table of calculated Raman-active combination frequencies was not drawn up; Table II gives the assignments for the observed Raman lines. The assignment of the 2201.40 and 2280.2 cm^{-1} lines, found by Glockler and Davis,[4] to the C^{13} isotope effect was suggested by Glockler and Renfrew.[5] This assignment agrees with calculated isotope shifts, as will be discussed below.

The doublet structures found by Glockler and Davis[4] in the 694 and 774 cm^{-1} lines are not inconsistent with the curves given by Placzek and Teller[14] for a parallel vibration, when allowance is made for the effect of the weaker Q branch. It must be remembered, however, that the theoretical curves should be compared only with *gas* phase data of fairly high resolution. In any case, this explanation is not applicable to the doublet in the 1448 cm^{-1} line, reported by Gredy,[6] since this line is depolarized and consequently of the perpendicular type.

The moderately strong intensity of the overtone at 2857 cm^{-1} is probably due to some resonance with the fundamental at 2916 cm^{-1}; this effect is observed in other compounds containing methyl groups.

Normal Coordinate Treatment

Approximate factoring

By using the symmetry of the molecule, the secular equation for the internal vibrations can be factored into one cubic and three quartic factors (Table III). Each of these factors contains a C−H stretching frequency of 2900–3000 cm^{-1}; by an appropriate choice of the symmetry coordinates used to set up the secular equation, these frequencies may be approximately factored off, and the problem reduced to one quadratic and three cubic equations.[15] This approximation was found to be accurate to within 2 cm^{-1} for all frequencies, and the reduction of the order of the factors effected a great saving of labor.

Potential function

A valence-force potential function, including interaction terms, was used. The bond distances

Table IV. *The fundamental frequencies of dimethyl acetylene, observed and calculated, in* cm^{-1}.

	Obs.	Calc.	Error %	Force constants involved†
A_1:	725	722*	−0.4	$(K_C+\frac{1}{2}k_{CC})$, k_{CA}, $[k_{C\gamma}]$
	1380	1402	+1.6	$[H_\alpha, H_\beta, h_{\alpha\beta}, k_{C\gamma}]$
	2270	2273*	+0.1	$[K_A]$, k_{CA}
	2916	2904	−0.4	$[K_H]$
$\bar{A}_2$:	1126	1124*	−0.2	$(K_C-\frac{1}{2}k_{CC})$, $[k_{C\gamma}]$
	1380	1402	+1.6	$[H_\alpha, H_\beta, h_{\alpha\beta}, k_{C\gamma}]$
	(2976)	2904	(−2.4)	$[K_H]$
E:	213	214*	+0.5	$(H_\varphi+\frac{1}{2}h_{\varphi\varphi})$
	1050	1036	−1.3	$[H_\beta]$
	1468	1476	+0.5	$[H_\alpha, H_\beta, h_{\alpha\beta}]$
	(2976)	3019	(+1.4)	$[K_H]$
$\bar{E}$:	371	370*	−0.3	$(H_\varphi-\frac{1}{2}h_{\varphi\varphi})$
	1029	1040	+1.1	$[H_\beta]$
	1448	1476	+1.9	$[H_\alpha, H_\beta, h_{\alpha\beta}]$
	2966	3019	+1.8	$[K_H]$

* These frequencies were used to adjust the unknown force constants K_C, k_{CC}, k_{CA}, H_φ, and $h_{\varphi\varphi}$.
† Force constants adopted from C_2H_6 and C_2H_2 are in brackets, [ ].

[13] S. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).
[14] G. Placzek and E. Teller, Zeits. f. Physik **81**, 209 (1933).
[15] B. L. Crawford, Jr., and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939). The method used to find the appropriate symmetry coordinates was developed in collaboration with Professor E. B. Wilson, Jr.; it will be described in a future publication.

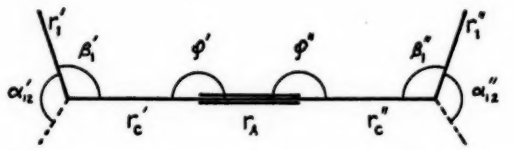

FIG. 4. Potential energy variables for dimethyl acetylene. Dotted lines indicate projections of C−H bonds r_2', r_3', r_2'', r_3'', on the plane of the paper. Equilibrium values of α_{ij}', α_{ij}'', β_i', β_i'', are all 109° 28′, the tetrahedral angle.

and valence angles used are shown in Fig. 4. The equilibrium values were assumed to be the same as the corresponding ones in methyl acetylene;[16, 17] the values adopted were: C−H, 1.093, C−C, 1.462, C≡C, 1.204A, with tetrahedral angles in the CH_3 groups.

The assumption was made that the part of the potential function pertaining to the CH_3 groups would be the same as in ethane, *except* that interactions between the two CH_3 groups would be negligible in dimethyl acetylene because of their greater separation. Accordingly, the potential function used by Stitt[18] was adopted, the interactions between methyl groups being omitted. This gave the following:

$$2V_1 = K_H \sum_6 (\Delta r_i')^2 + H_\alpha r_1^2 \sum_6 (\Delta\alpha_{ij}')^2 + H_\beta r_1^2 \sum_6 (\Delta\beta_i')^2 + h_{\alpha\beta} r_1^2 \sum_{12} (\Delta\beta_i')(\Delta\alpha'_{i,\, i\pm1}) + k_{C\alpha} r_1 \sum_6 (\Delta r_C')(\Delta\alpha_{ij}') + k_{C\beta} r_1 \sum_6 (\Delta r_C')(\Delta\beta_i'),$$

where $i=1, 2, 3$, and the summations are taken over both $'$ and $''$ variables. (The number of terms in each summation is indicated.) The force constants $k_{C\alpha}$ and $k_{C\beta}$ always appear as $(k_{C\alpha}-k_{C\beta})=k_{C\gamma}$. The values of these five "methyl group" constants (Table V), were taken from Stitt's[18] results. Inasmuch as the C−C bond in dimethyl acetylene is not the same as that in ethane, the use of this value for $k_{C\gamma}$ is somewhat arbitrary.

The remaining part of the potential function used is similar to that used for acetylene:[19]

$$2V_2 = K_A(\Delta r_A)^2 + K_C[(\Delta r_C')^2 + (\Delta r_C'')^2] + k_{CC}(\Delta r_C')(\Delta r_C'') + k_{CA}(\Delta r_A)[(\Delta r_C') + (\Delta r_C'')] + H_\varphi r_C^2[(\Delta\varphi')^2 + (\Delta\varphi'')^2] + h_{\varphi\varphi} r_C^2 (\Delta\varphi')(\Delta\varphi'').$$

TABLE V. *Force constants involved in dimethyl acetylene.*

CONSTANT	TYPE	VALUES (10^5 DYNES/CM)	COMPARISON VALUE
K_H	C−H stretching	4.79*	
H_α	HCH angle bending	0.46*	
H_β	HCC angle bending	0.55*	
$h_{\alpha\beta}$	angle interaction	+0.02*	
$k_{C\gamma}$	C−C stretching—angle interaction	−0.47*	
K_A	C≡C stretching	15.587†	
K_C	C−C stretching	5.18₃	4.50*
k_{CC}	C−C bond interaction	+0.38₆	
k_{CA}	C−C, C≡C interaction	+0.44	
H_φ	C≡C−C bending	0.155	0.2096†
$h_{\varphi\varphi}$	angle interaction	+0.134	+0.1567†

* Values from C_2H_6, Stitt (reference 18).
† Values from C_2H_2, Colby (references 19 and 20).

The force constant for the acetylenic bond, K_A, was taken to be the same as in C_2H_2 (Table V). The other constants were regarded as unknowns to be evaluated from the observed frequencies.

The observed shortening of the C−C single bond with respect to that in ethane[16, 17] has certain implications regarding the force constants K_C and k_{CC}. In qualitative agreement with Badger's rule, we should expect K_C to be greater than in C_2H_6. Moreover, if we regard this shortening as evidence of contributions from allenic structures such as:[17]

$$H_3C-\overset{(+)}{C}=C=\overset{(-)}{C}H_3,$$

we should expect k_{CC} to be fairly large, and positive. The sign follows from the fact that contraction of r_C' will favor an allenic structure involving a single bond at r_C''; this single-bond character will in turn favor an *extension* of r_C''. Hence the potential energy should be lower when $\Delta r_C' = -\Delta r_C''$, and this implies that k_{CC} is positive.

[16] G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem. **41**, 123 (1937).
[17] L. Pauling, H. D. Springall and K. J. Palmer, J. Am. Chem. Soc. **61**, 927 (1939).
[18] F. Stitt, J. Chem. Phys. **7**, 297 (1939). Dr. Stitt's notation differs somewhat from ours. His K_H, K_α, K_β, $K_{\alpha\beta}$, $K_{c\alpha}$, and $K_{c\beta}$ correspond to our K_H, H_α, H_β, $k_{\alpha\beta}$, $k_{C\alpha}$, and $k_{C\beta}$, respectively.
[19] W. F. Colby, Phys. Rev. **47**, 388 (1935).

Results of calculations

The force constants finally adopted are given in Table V; the frequencies calculated from them are compared with the observed values in Table IV. The last column in Table IV lists, opposite each frequency, the force constants which have an appreciable effect on that frequency. Thus, in the E factor, the constants H_φ and $h_{\varphi\varphi}$ will control the lowest frequency (213 cm^{-1}), but the three higher frequencies will change by a wave number or two at most, for the maximum range of possible values of these constants.

The agreement of the calculated frequencies with the observed is quite good. In the case of the frequencies marked with an asterisk in Table IV, this agreement is not significant: five force constants are determined from five known frequencies. The other ten frequencies, however, are determined by constants *which were transferred from another molecule* (ethane); the excellent agreement obtained (maximum error 1.9 percent) lends support to the idea that valence-force potential constants have a real physical meaning, and can be transferred from one molecule to another in cases where similar structures are involved. The agreement of the rocking frequencies in the E and $\bar{E}$ factors (1036 and 1040 cm^{-1}, calculated) is especially pleasing. The corresponding frequencies in ethane (830 and 1200 cm^{-1}) are quite different; yet the ethane force constants give the correct frequencies for dimethyl acetylene.

The values of K_C and k_{CC} accord with the *a priori* considerations given above. The comparison between the bending constants H_φ and $h_{\varphi\varphi}$ (C≡C−C angles) with the corresponding constants in acetylene (C≡C−H angles) is given in Table V in terms of *linear* constants. Alternatively, we may express the potential function for such distortions in terms of *angular* constants; i.e., the terms in V_2 involving $(\Delta\varphi')$ and $(\Delta\varphi'')$ will be

$$H_\varphi'[(\Delta\varphi')^2+(\Delta\varphi'')^2]+h_{\varphi\varphi}'(\Delta\varphi')(\Delta\varphi''),$$

instead of those given above. The comparison now becomes:

	C_4H_6	C_2H_2
H_φ'	0.331	0.234
$h_{\varphi\varphi}'$	+0.286	+0.175

where H_φ' and $h_{\varphi\varphi}'$ are in units of (10^{-11} erg/radian^2).[20] The two apparently discordant comparisons are of course in agreement when the physical meanings of the two types of bending constant are considered.

The effect of the C^{13} isotope can be calculated from the normal coordinate treatment. The observed effect (see Table II) is complicated by the resonance splitting of the expected 2270 cm^{-1} Raman line. We may calculate[21] the isotopic shift for each of the unsplit levels separately, however; the mean of these shifts should agree with the mean of the observed isotopic shifts. The A_1 fundamental at 2270 cm^{-1} should be shifted by 46.4 cm^{-1}. The $\bar{A}_2$ fundamental at 1126 cm^{-1} should be shifted by 12.8 cm^{-1}; if we neglect anharmonic forces, its overtone should be shifted by 25.6 cm^{-1}. The mean of 46.4 and 25.6 gives us an expected mean shift of 36.0 cm^{-1}; the mean of the observed shifts is 32.8 cm^{-1}.

In concluding, I wish to express my thanks to Professor G. B. Kistiakowsky for the loan of the material studied, and to Professor E. B. Wilson, Jr., for proposing this research and for contributing many helpful suggestions to its progress.

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[20] The values given for C_2H_2, here and in Table V, were recalculated from Colby's formulas (reference 19). Colby used the values 1.08 and 1.19A for the C−H and C≡C distances, respectively; we have used 1.057 and 1.204A. This change will not affect the force constants for the linear vibrations of C_2H_2. It should be noted that in the nonlinear part of the C_2H_2 potential function, our H_φ' is equal to Colby's K_1, while our $h_{\varphi\varphi}'=2K_2$ in his notation.

[21] For the method used in calculating the isotope shifts, see reference 14, page 229.

The Infra-Red Absorption Spectrum of Methylamine Vapor

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AND
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(Received May 12, 1939)

The infra-red absorption of methylamine vapor has been measured from 2 to 18μ with a cell of 18 cm length using pressures from 2 to 55 cm. A total of nineteen bands has been observed, nine of which are assigned to fundamental vibrations. The bending vibrations of the two groups give rise to several bands in the region from 6 to 8μ. This causes considerable overlapping which makes it difficult to locate band centers and to determine band types in this region. Three bands which originate from the C−H vibrations occur at wave-lengths between 3.0 and 3.6μ. A band due to the N−H parallel valence vibration has been found at 2.98μ. The most intense band in the spectrum occurs at 12.9μ, and arises from a bending vibration of the hydrogen atoms in the amino group. The parallel vibration between the methyl and amino groups gives rise to an intense band at 9.56μ. This is a parallel band having a sharp and intense zero branch. A band also due to a bending vibration in the amino group was observed at 16μ, and from the experimental curve it can not be said whether it is parallel or perpendicular; hence definite assignment is not made. The other bands which have been observed have been assigned to overtones and combinations.

INTRODUCTION

PREVIOUS studies on methylamine have been confined largely to the region less than 2μ. Kohlrausch[1] has studied the Raman spectrum of aqueous methylamine, and the liquid has been studied by other workers. The assignments for the valence vibrations were $\nu_{C-H}=3000$ cm^{-1}, $\nu_{N-H}=3350$ cm^{-1}, and $\nu_{C-N}=1040$ cm^{-1}. M. Freymann[2] has studied the region from 0.8μ to 1.2μ and found two absorption bands at about 1.042, and 1.001μ. The more intense band at 1.042μ was attributed to $3\nu_{NH}$. It was thought that a study of the infra-red spectrum to 20μ would make it possible to discover a large number of the fundamentals, and thus relate the infra-red absorption spectrum to the modes of vibration of the molecule. The spectrum should not vary greatly from that of methyl alcohol, which has been recently studied by Borden and Barker,[3] except for the bands due to absorption by the amino group.

EXPERIMENTAL METHOD

A study has been made of the infra-red absorption of methylamine vapor in the region from 2–18μ by means of a prism instrument with prisms of fluorite and sylvine; and the regions of more intense absorption have been studied in detail by employing a grating spectrometer of good resolution. The fore prism of the grating spectrometer was of rocksalt. In the region beyond 16μ the intensity was so low that the grating instrument could not be used. For the region between 2μ and 5.5μ a 4812-lines-per-inch grating, having a ruled surface of five inches, was available, while the grating for the region from 5.5μ to 13μ was of the same size and had 2060 lines per inch. The effective slit width varied from 6 cm^{-1} in the 2μ region to 1.4 cm^{-1} in the 13μ region. A Nernst glower was used as the source of radiation, and a thermocouple in conjunction with a Moll thermorelay was used as a detector. The general features of the grating spectrometer were like those of the instrument of Meyer[4] and will not be described. A glass cell of 18 cm length with rocksalt windows was used to contain the gas. Various pressures from 2 to 60 cm were employed in studying the bands in the different regions.

The methylamine vapor was obtained from Kahlbaum, in the form of an anhydrous liquid.

* This paper is based upon results forming part of the dissertation submitted by A. P. Cleaves to Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. An abstract has been published by the authors in the Bulletin of the American Physical Society (No. 14), April (1939).

[1] K. W. F. Kohlrausch, Monatshefte für Chemie (Wien) **68**, 349 (1936).

[2] M. Freymann, Comptes rendus **202**, 1674 (1936).

[3] A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).

[4] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

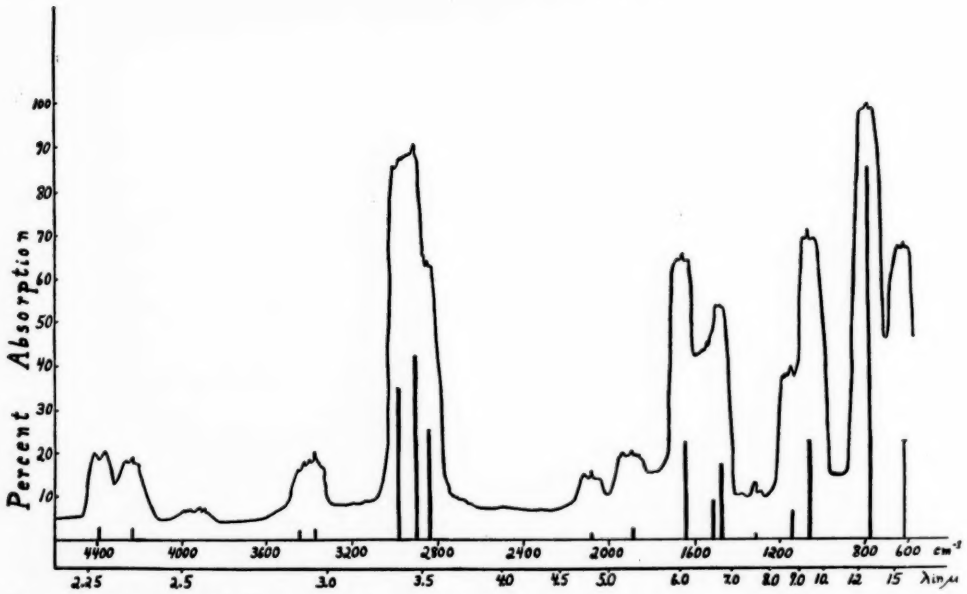

FIG. 1. Infra-red absorption by methylamine vapor from 2.2μ to 18μ at pressures from 2 to 55 cm in an 18-cm cell. The vertical lines indicate the relative intensities of the bands.

It was then triply distilled and silica gel was used as a drying agent. After each condensation any remaining volatile material was pumped away. The most likely impurity would be ammonia, but as no band was observed at 950 cm^{-1}, which is a strong NH_3 absorption region, it was concluded that this impurity was not present in appreciable amounts.

RESULTS

The region of general absorption by methylamine vapor from 2.2 to 18μ are shown in Fig. 1. The region from 1.8 to 2.2μ was also surveyed and several weak bands were observed. Since these bands arise from harmonics or combinations and fall in a region where a grating of good resolution was not available, these bands were not studied in detail. The vertical lines under these bands represent the absorption reduced to a pressure of 3 cm in the cell. In the actual drawing the absorption in the weaker bands has been exaggerated. The band at 12.9μ is the most intense one in the entire spectrum. In Fig. 1 is shown a total of 19 bands. The two very weak bands at about 4000 cm^{-1} are due to combinations, and the stronger bands at about 4200 and 4400 cm^{-1} are also due to combinations. The details as to the assignment of the modes of vibration will appear in the discussion. Also the structure of these bands obtained by a detailed study is shown in Figs. 2–8. In Table I is given the frequency, wave-length, effective slit width, pressure of gas, and the assigned mode of vibration of each band.

TABLE I. *The positions of the observed bands, pressures, effective slit widths, and assignments of vibrations.*

WAVE NUMBERS	MICRONS μ	PRESSURE CM HG	EFFECTIVE SLIT CM^{-1}	ASSIGNMENT*
4385	2.278	40	6	$\begin{cases}\nu_{CH}\perp+\delta_{CH}\parallel \\ 3\delta_{CH}\perp^{(2)}\end{cases}$
4226	2.370	40	6	$\begin{cases}\nu_{CH}\parallel+\delta_{CH}\parallel \\ \nu_{CH}\parallel+\delta_{CH}\perp^{(2)}\end{cases}$
3470*R*				$\nu_{NH}\perp$
3425	3.080	55	5	Probably combinations
3360	2.976	55	5	$\nu_{NH}\parallel$
2968	3.370	3	5	$\nu_{CH}\perp$
2895	3.45	3	5	$2\delta_{CH}\perp^{(2)}$
2819	3.55	3	5	$\nu_{CH}\parallel$
2072	4.83	50	4	$2\nu_{CN}\parallel$
1814	5.52	40	4	$\delta_{NH}\parallel^{(1)}+\nu_{CN}\parallel$
1625	6.15	4	3.5	$\delta_{NH}\perp^{(2)}$
1516	6.60	10	3	$2\delta_{NH}\parallel^{(1)}$
1460	6.85	7	3	$\delta_{CH}\perp^{(2)}$
1426	7.02	7	3	$\delta_{CH}\parallel$
(1312)?	7.62	45	3	$\delta_{CH}\perp^{(1)}$
1127	8.88	20	2.5	$\delta_{NH}\parallel^{(2)}$?
1045	9.56	4	2.0	$\nu_{CN}\parallel$
783	12.92	2	1.4	$\delta_{NH}\parallel^{(1)}$
630	16	20	8	$\delta_{NH}\perp^{(1)}$ or $\delta_{NH}\parallel^{(2)}$

* Different vibrations of the same type are denoted by superscripts on the right side.

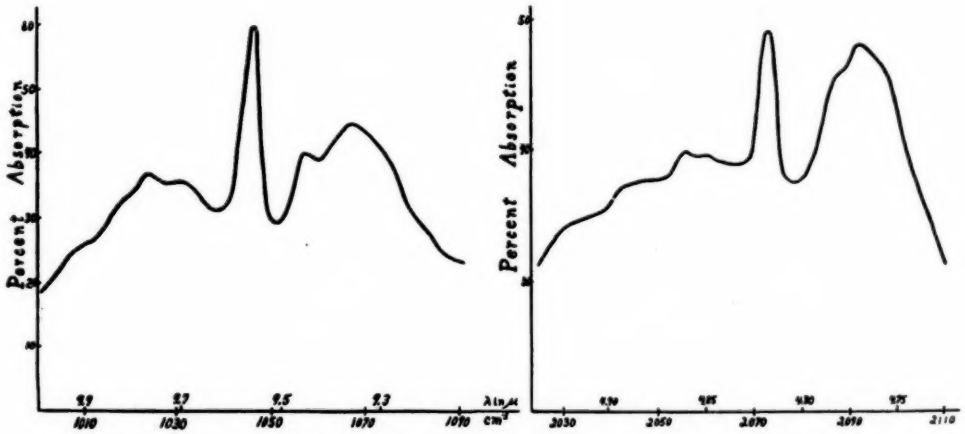

FIG. 2. The $\nu_{CN}||$ vibration at 1045 cm^{-1} and its first harmonic $2\nu_{CN}||$ at 2072 cm^{-1}.

DISCUSSION OF RESULTS

The form of the methylamine molecule is known from stereochemical data, from electron diffraction[5] measurements, from Raman[1] and photographic infra-red[6, 7] spectra of gaseous and liquid methylamine and of its solutions and from corresponding data on similar molecules. From all these data there is evidence that the methyl group angles are approximately tetrahedral, that the C−H distances are of the same magnitude as in methane (1.1×10^{-8} cm), that the C−N−H angles are about 108° and that $r_{CN}=1.47$A and $r_{NH}=1.02$A. The molecule is in reality an asymmetrical top, but the asymmetry is only slight as in methyl alcohol[3] so that it can (approximately) be treated as a symmetric top with a symmetry axis lying along the C−N bond. The only symmetry element which is preserved when considering the molecule as an asymmetric top, is a plane through the figure axis (C−N) and through one of the H atoms. The moment of inertia about the figure axis is approximately $C=8\times10^{-40}$ g cm^2, and the average value of the two larger moments of inertia A and B, which are very similar, is about 38×10^{-40}.[6]

The methylamine molecule possesses 15 fundamental vibrations. Since it is an asymmetric top all of these vibrations are allowed and so should occur in the infra-red, but some vibrations, such as perpendicular ones in CH_3, may retain their degeneracy, so that less than 15 frequencies may be observed. Of the nineteen bands found in the near infra-red in the present research eleven have been assigned to the fundamental modes of motion, two of these tentatively. The difference in these numbers arises from the fact that three of the assigned frequencies are likely to be doubly degenerate, and the 15th fundamental frequency has been observed only in the Raman spectrum.[8] The remaining eight bands have been assigned to overtones and combinations.

THE C−N VIBRATION

One of the strongest bands in the spectrum appears at 9.57μ corresponding to a frequency of 1045 cm^{-1}. It has the shape of a parallel band (see Fig. 2), and corresponds to the parallel vibration between the methyl and amino groups. It has very nearly the same frequency as that found for the CH_3-OH vibration in CH_3OH at 1034 cm^{-1} and corresponds closely to 1048 cm^{-1} for CH_3-F. This is due to similarity of the masses of fluorine and the amino group. The band at 1045 cm^{-1} has very recently been simultaneously reported by Owens and Barker,[9] who, with an instrument with greater resolving power in this region than that used in this work, were able to obtain the fine structure of this band.

The 1045 cm^{-1} band has its first harmonic at 4.83μ or 2072 cm^{-1} giving an anharmonicity of

[5] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[6] H. W. Thompson and H. A. Skinner, J. Chem. Phys. **6**, 775 (1938).
[7] M. & R. Freymann, J. de phys. et rad. **4**, 476 (1936).
[8] J. S. Kirby-Smith and L. G. Bonner, Bull. Phys. Soc. April (1939).
[9] R. G. Owens and E. F. Barker, Bull. Am. Phys. Soc. 14, April (1939).

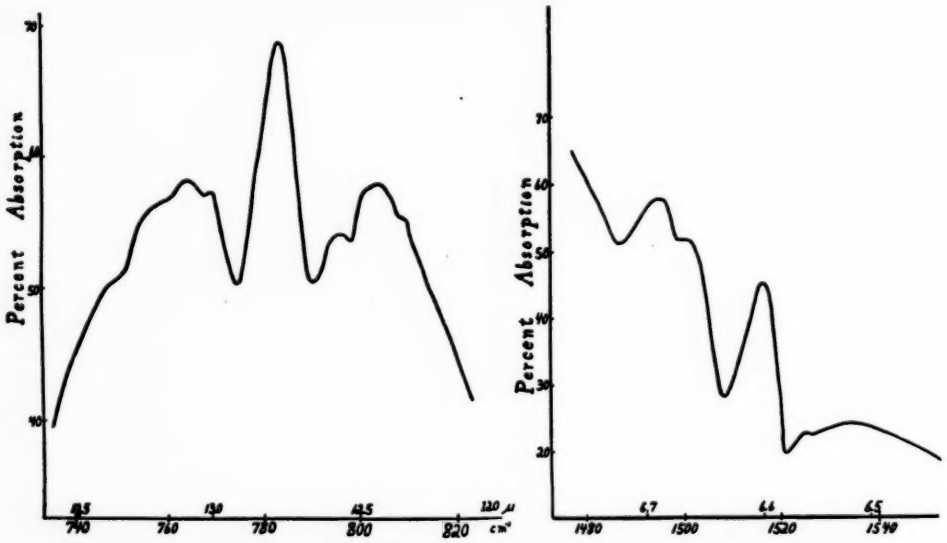

FIG. 3. The $\delta_{NH}||^{(1)}$ vibration at 783 cm^{-1} and its first harmonic $2\delta_{NH}||^{(1)}$ at 1516 cm^{-1}.

9 cm^{-1}. This small value is reasonable for this type of vibration. The harmonic is shown in Fig. 2 and resembles very much the overtone at 2054 cm^{-1} of the 1034 band in methyl alcohol.

THE AMINO VIBRATIONS

The band at 12.92μ corresponding to a frequency of 783 cm^{-1} is the most intense in the entire spectrum. The low frequency suggests a bending vibration. Since it is of the parallel type, the change of the electric moment must lie in the direction of the C—N axis. A vibration which has this characteristic and which should have a low frequency, is one in which the H atoms in the NH_2 group move perpendicular to the N—H bonds and almost parallel to the figure axis of the molecule on account of the C—N—H angle. The hydrogens in this vibration move jointly in a group. Although the corresponding band has not been found in the infra-red spectrum of CH_3OH, we would like to make this assignment.

The harmonic of the 783 cm^{-1} band is the parallel band located at 1516 cm^{-1} having an anharmonicity of 25 cm^{-1} which is a reasonable value. The band is reproduced also in Fig. 3. The strong absorption in the *P* branch region is caused by overlapping absorption of the 1450 cm^{-1} region.

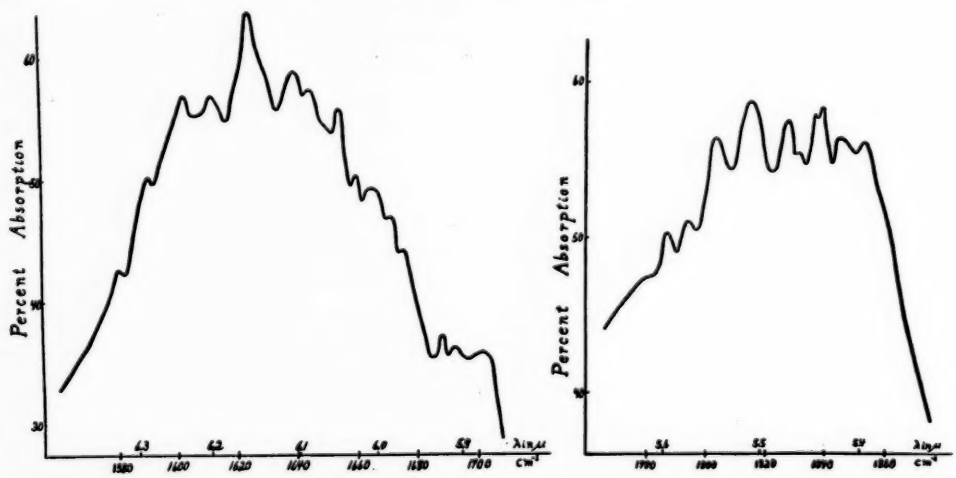

FIG. 4. The $\delta_{NH}\perp^{(2)}$ vibration at 1625 cm^{-1} and the combination band $\delta_{NH}||^{(1)}+\nu_{CN}||$ at 1814 cm^{-1}.

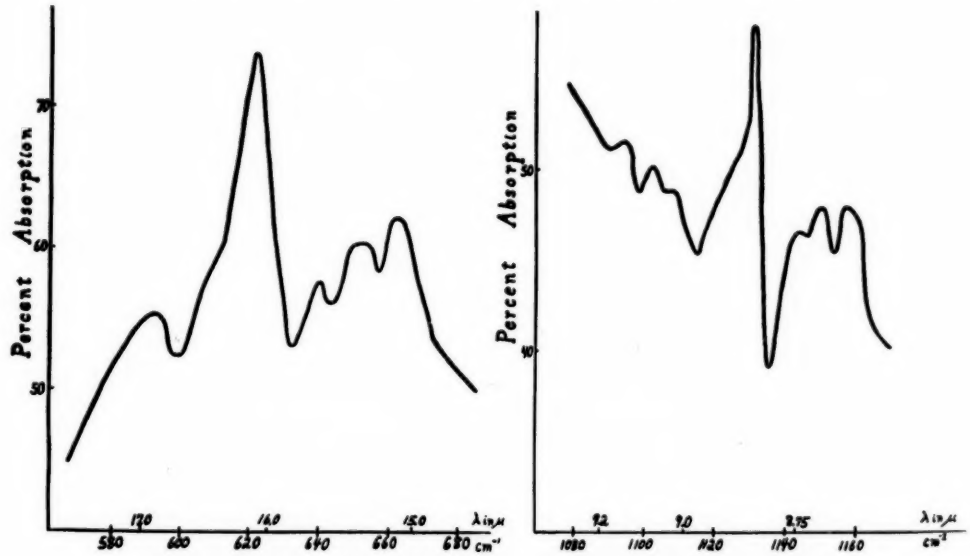

FIG. 5. The absorption in the 620 cm^{-1} region and the 1127 cm^{-1} band.

There is a probability that the combination frequency of 783 cm^{-1} and 1045 which should occur rather strongly can be correlated with the band at 5.52μ or 1814 cm^{-1}.

Another bending vibration should arise from a motion of the two H atoms moving towards each other perpendicular to the N—H bonds as in the $\delta_i||$ (1595 cm^{-1}) vibration of H_2O. However, while this vibration results in a change in electric moment parallel to the figure axis in H_2O, it gives in the case of methylamine a strong component perpendicular to the C—N axis because of the angle C—N—H. Looking for a band in this region it seems that the band at 1625 cm^{-1} would give the best fit in frequency. It is presented in Fig. 4 and certainly resembles a parallel type band more than a perpendicular one. However, there is serious overlapping in this region which may arise due to combinations of 1045 and 630 cm^{-1}.

Two other types of motion in the NH_2 group consist of the hindered rotation and a bending

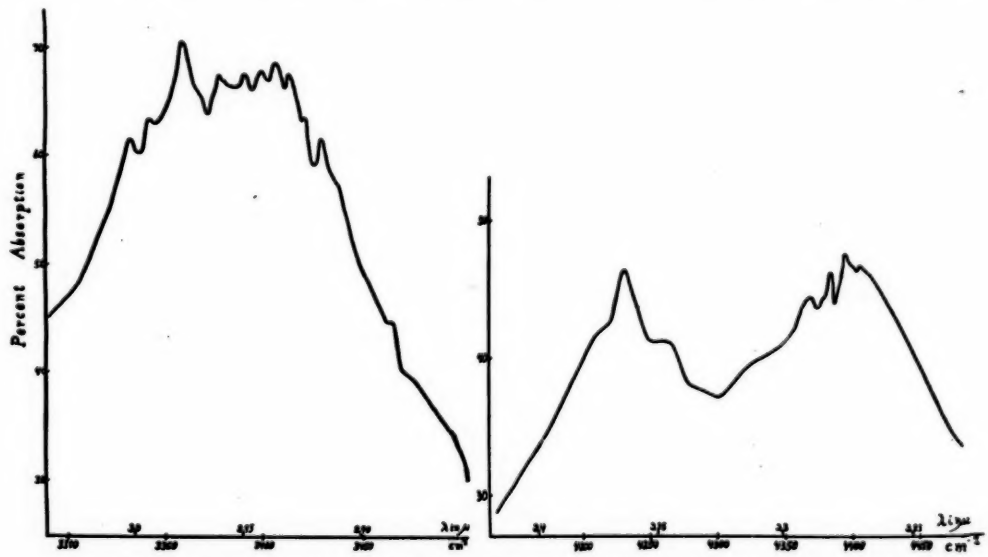

FIG. 6. The $\nu_{NH}||$ vibration at 3360 cm^{-1} and combination bands at higher frequencies.

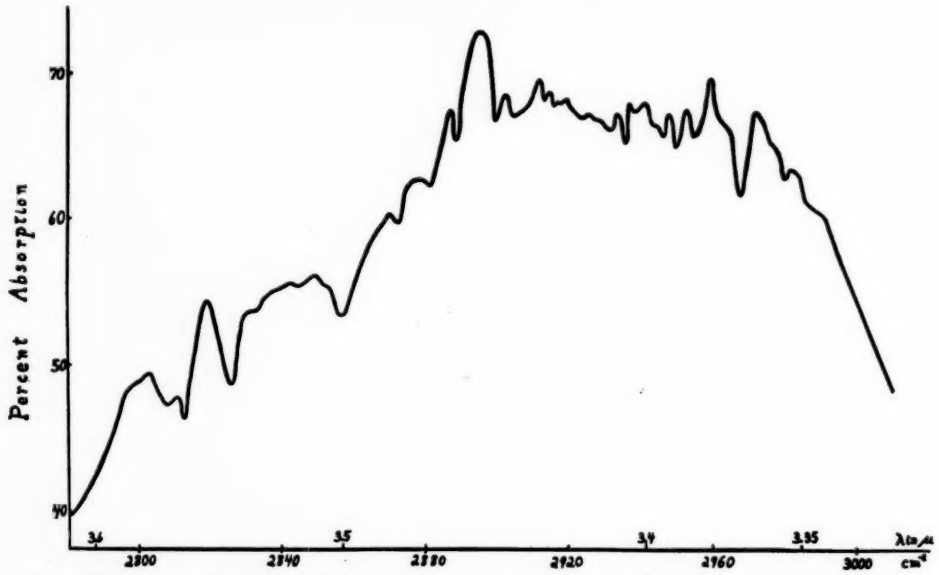

FIG. 7. The $\nu_{CH}||$ vibration at 2819 cm^{-1}, the $\nu_{CH}\perp$ vibration at 2968 cm^{-1}, also the harmonic $2\delta_{CH}\perp^{(2)}$ at 2895 cm^{-1}.

vibration which consists of an oscillation of the hydrogen atoms perpendicular to the N−H bonds, a sort of twisting motion, giving a change of the electric moment with its major component parallel to the figure axis. The motion is similar to the one for the 783 cm^{-1} frequency with the only difference that the two hydrogen atoms are now moving in opposite directions. The frequencies of the two bands associated with these vibrations would no doubt be low. Unfortunately the low frequency region was studied only with a sylvine prism, and the results could not be carried beyond the region of 18μ. An absorption band was observed which extended from 680 cm^{-1} to 570 cm^{-1}. The graph shown in Fig. 5 indicates a parallel type of band. When measured at high pressures the band developed a second rather narrow branch not as intense as the main branch, and spaced about 20 cm^{-1} toward higher wave numbers from it; so that from the experimental data it cannot be clearly stated whether this is a parallel or a perpendicular band. The parallel band at 1127 cm^{-1} is shown in Fig. 5. If this were a fundamental, it would have to be associated with the N−H twisting vibration described above, however, we are aware that our investigation has been limited in the low frequency region.

The region of the N−H valence vibration shows an unexpected feature. While there is no doubt that the band at 3360 cm^{-1} must be associated with the vibration $\nu_{NH}||$ there is no evidence for the perpendicular vibration which from Raman measurements[8] in gaseous methylamine is fixed at 3470 cm^{-1}. Since $\nu_{NH}||$ is very strong in the Raman effect and $\nu_{NH}\perp$ is very weak, one would expect a strong infra-red band corresponding to the frequency of the latter vibration. It can be seen from Fig. 6 that no strong absorption occurs at the expected position. Instead there is a weaker band at 3425 cm^{-1}, but it is possible that the whole region from 3390 to 3430 cm^{-1} consists of overlapping absorption of different combination bands. So far no explanation can be given as to why the perpendicular N−H valence vibration is missing, but we should like to mention that the same is true for NH_3 where this vibration is calculated from overtones and combinations.

THE C−H VIBRATIONS

The valence vibrations along the CH bonds give rise to two bands at 3.55μ and 3.37μ corresponding to the parallel vibration of the three hydrogens, $\nu_{CH}||$ (2819 cm^{-1}). The results are shown in Fig. 7. There is indication of some resolution in the latter band's P and R branches. It is a doubly degenerate vibration as in methyl

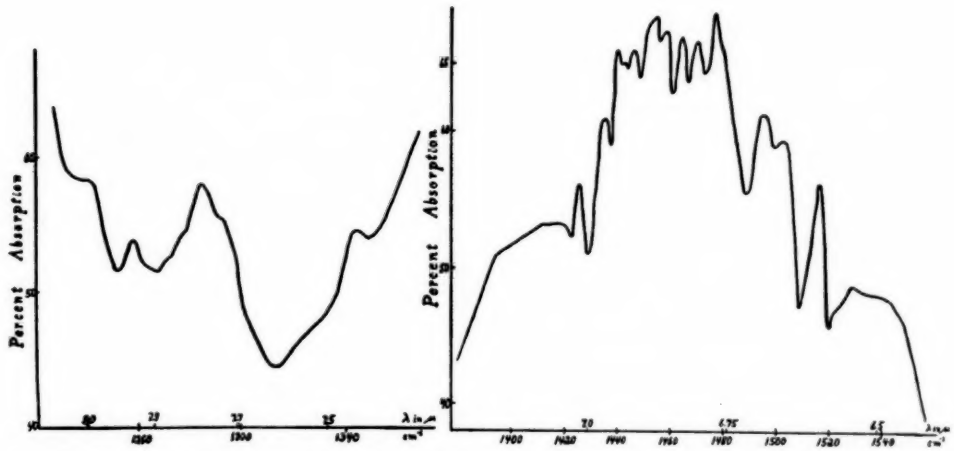

FIG. 8. The $\delta_{CH}||$ vibration at 1426 cm^{-1}, the $\delta_{CH}\perp^{(2)}$ vibration at 1460 cm^{-1}, the $2\delta_{NH}||^{(1)}$ harmonic at 1516 cm^{-1}, and the $\delta_{CH}\perp^{(1)}$ vibration at 1312 cm^{-1}.

alcohol, the degeneracy probably not being removed on account of the very small deviation of the molecule from being a symmetric top.

As is characteristic for the methyl group in many compounds, particularly the methyl halides, another strong band appears in the same region, that is in CH_3NH_2 at 3.45μ or 2895 cm^{-1}. In these mentioned cases this band has been interpreted as being an overtone of the higher frequency perpendicular CH_3 bending vibration intensified by an interaction with $\nu_{CH}||$. The same explanation can be applied here.

The fundamental vibration 1460 cm^{-1} $\delta_{CH}\perp^{(2)}$ involved in the last discussed band is the most intense band in the 7μ region, partially resolved, and shown in Fig. 8. It is somewhat similar in contour to the trace of the perpendicular band at 9940A which is reported in the photographic region.[6] By analogy with this band the center is chosen at 6.85μ or 1460 cm^{-1}, a value which makes the suggested interaction seem reasonable. In the Raman effect[8] a broad line has been observed at 1460 cm^{-1} possibly due to the superposition of two lines. A weaker parallel band found at 7.02μ (1426 cm^{-1}) may be assigned to the parallel deformation vibration, $\delta_{CH}||$. The corresponding bands in methyl alcohol have been located at 1477 and 1455 cm^{-1}. The other perpendicular CH_3 bending vibration has been assigned in CH_3OH to a band at 1340 cm^{-1}. There is no definitely perpendicular band in that region that could be assigned unambiguously to this vibration unless one considers the remote possibility of associating the minimum at 1312 cm^{-1} with the center of a band.

It seems reasonable to mention the perpendicular band at 2.278μ (4385 cm^{-1}) and the parallel band at 2.37μ (4226 cm^{-1}), shown in Fig. 6, in connection with the C−H frequencies. No unambiguous explanation can be given for these bands since several combinations seem possible. The following pairs would account for the bands in question: 2968+1426 ($\nu_{CH}\perp+\delta_{CH}||$), 2820+1426 ($\nu_{CH}||+\delta_{CH}||$) and $3\times1460=4380$ ($3\delta_{CH}\perp^{(2)}$) and

$$2820+1460=4280\ (\nu_{CH}||+\delta_{CH}\perp^{(2)}).$$

The second pair corresponds to a suggestion by Adel and Barker,[10] based upon the interaction between the levels involved.

In conclusion, it should be emphasized that a good agreement of the assigned frequencies with the possible modes of vibration has been reached. On account of the overlapping of some bands not all frequencies could be identified with the same certainty. The writers wish to express their appreciation to Dr. H. Sponer of Duke University for many helpful suggestions in the interpretation of the results. The research was supported in part by a grant to her from the Duke University Research Fund.

[10] A. Adel and E. F. Barker, J. Chem. Phys. **2**, 627 (1934).

Intensities of Electronic Transitions in Molecular Spectra

VIII*a*. Odd-Numbered Conjugated Polyene Chain Molecules and Organic Dyes (with notes on optical anisotropy and Raman intensities)

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Using the Hückel *LCAO* molecular orbital approximation, it is found that the lowest excited electronic levels, long wave-length electronic spectra, and so on, should show exactly the same special features for conjugated polyene chain molecules with an *odd* as for those with an *even* number of atoms in the conjugated chain. Examples of even-numbered conjugated chain molecules are the carotenoids, discussed previously. Many dye molecules (for example, certain infra-red sensitizers) are salts whose positive ion is built on an odd-numbered conjugated chain with a nitrogen atom terminating the chain at each end. It seems probable that the explanation of the spectra of these dyes is essentially similar to that of the carotenoids, although much remains to be done toward understanding the effect of phenyl and other unsaturated groups when included in the conjugated chains. Absorption and refraction of carotenoid crystals are briefly discussed; the predicted strong pleochroism and double refraction are known experimentally. Bearing of the papers of the present series on Raman intensities of conjugated chain molecules is briefly discussed. A correction is given of an error in papers VI and VII of this series.

I. INTRODUCTION: EVEN CONJUGATED POLYENES

IN some recent papers,[1] the writer has discussed the unsaturation-electron spectra of conjugated dienes and polyenes (e.g. $CH_2=CH-CH=CH\cdots=CH_2$). In these molecules, there is a chain of n atoms with n unsaturation electrons and $n/2$ double bonds, n being an even number.

In terms of the *MO* (molecular orbital) approximation, there exist n unsaturation *MO*'s, of which $n/2$ are more or less bonding. In the normal state N of the molecule, each of these bonding orbitals is occupied by a pair of electrons.

There also exist $n/2$ unsaturation *MO*'s which are more or less antibonding. Excited states of the molecules, designated T and V states, are obtained by exciting one electron from any one of the $n/2$ normally occupied unsaturation *MO*'s into any one of the $n/2$ normally unoccupied ones. This gives a total of $n^2/4$ T states and $n^2/4$ V states. The T are triplet and the V are singlet states; only the latter are important spectroscopically. In order of increasing energy, the V states are labeled V_1, V_2, V_3, and so on.

The longest wave-length electronic transition of appreciable intensity in absorption is then $N\rightarrow V_1$. This shifts to longer wave-lengths with increasing n. The calculations showed that if the polyene chain has the most elongated possible form (*trans, trans, trans,* $\cdots$), the $N\rightarrow V_1$ transition should be far stronger than all the other $N\rightarrow V$ transitions together, and its strength should increase with the length of the chain. This calculated result is paralleled by experimental data on the polyenes, especially the carotenoids.[1] The calculations showed that for less elongated (more *cis*-like) molecules, the intensity of $N\rightarrow V_1$ should be reduced in favor of $N\rightarrow V_2$, $N\rightarrow V_3$, and so on. A further point of interest was that the $N\rightarrow V_1$ transition in molecules of the most elongated form should be polarized approximately along the long axis of the molecules.

II. ODD CONJUGATED POLYENES

There is an important class of molecules,[2] including many dyes, whose simplest prototypes

[1] R. S. Mulliken, J. Chem. Phys. **7**, 121, 384 (1939): III, VII of current series.

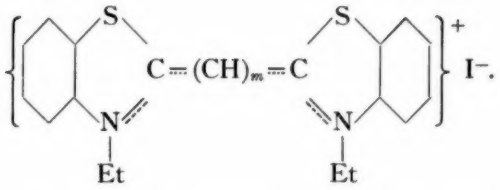
[2] The spectra of these have been discussed briefly from the *AO* (atomic orbital) point of view by Pauling in Gilman's *Organic Chemistry*, Vol. 2, p. 888. According to this viewpoint, the states here called N and V_1 are identified with the two states resulting from resonance between the two structures ($NH_2^+=CH\cdots CH-NH_2$) and ($NH_2-CH\cdots CH=NH_2^+$), and $N\rightarrow V_1$ belongs to the class of charge-transfer spectra (cf. J. Chem. Phys. **7**, 24, 122, 135 (1939)). But as a result of the present work, it seems that this viewpoint is less significant than at first appeared. For a comparison with the *MO* approximation indicates that the wave functions of states N and V_1 are not very adequately represented in the *AO* approximation by combinations just of the above two bond structures alone, but that other

are polyene chain molecules similar to those discussed in the preceding paragraphs except that the number n of atoms forming the conjugated chain is odd instead of even. In the commonest examples, the chain forms a positive ion such as $(NH_2\overline{\cdots}CH\overline{\cdots}CH\cdots CH\overline{\cdots}NH_2)^+$, where the $\overline{\cdots}$ indicates a bond structure most simply described as being a result of resonance between two forms $NH_2^+=CH\cdots CH-NH_2$ and $NH_2-CH\cdots CH=NH_2^+$.

In these odd-numbered polyene chain molecules, there are $n+1$ unsaturation electrons and $(n-1)/2$ double bonds. In terms of the *MO* approximation, there exist a total of n unsaturation *MO*'s just as when n is even. These have been discussed by Hückel and others.[3] In the normal state, $(n+1)/2$ of these *MO*'s are occupied each by a pair of electrons, while $(n-1)/2$ remain unoccupied. Excitation of one electron from any one of the $(n+1)/2$ occupied into any one of the $(n-1)/2$ unoccupied *MO*'s gives a T and a V state. The V states can be labeled V_1, V_2, V_3 and so on just as in the case when n is even. There are altogether $(n^2-1)/4$ V states here.

It is found by very simple calculations—and this is the main new point to be reported—that the intensity and other relations among the different $N\rightarrow V$ transitions are very similar for n odd to those for n even. Namely, if the chain has maximum elongation, the longest wave-length transition $N\rightarrow V_1$ is by far the strongest of the $N\rightarrow V$ transitions, while if it is more curled up, a considerable amount of intensity goes into $N\rightarrow V_2$, $N\rightarrow V_3$, etc.

Many dye molecules are salts whose positive ion is built on an odd-numbered polyene chain with nitrogen at each end. For example, the polycarbocyanine dyes, used as sensitizers in infra-red photography,[4] include types such as the following:



In this and other examples the simple polyene chain theory of course needs some elaboration to take account of additional unsaturation electrons present in attached phenyl groups, sulfur atoms, and so on. Nevertheless, it may reasonably be anticipated that when the structure is dominated by a conjugated polyene chain, the long wave-length spectrum will probably be essentially that of such a chain, as discussed above.

In case the structure of the molecule permits an elongated chain, the longest wave-length absorption maximum may probably be expected to be by far the strongest; but if the chain is more strongly bent or curled, other fairly prominent maxima at somewhat shorter wave-lengths may also be present. Further theoretical study will show more precisely what spectral modifications are to be expected from the presence of attached or inserted unsaturated rings or other groups in conjugated polyene chains.

III. Even Polyene Crystals

Calculations such as those discussed here have various applications not only to spectra but also to other optical properties of substances.[5] Consider for example a crystal built up of elongated conjugated polyene molecules aligned more or less parallel. The absorption coefficient in the $N\rightarrow V_1$ region, and the refractive index at longer wave-lengths, should be much higher for light with electric vector vibrating parallel to the long molecule-axes than for light polarized in either of the directions perpendicular to this. From a conversation with Dr. S. B. Hendricks, the writer has learned that crystals of the carotenoid methylbixin do indeed show exactly this behavior.[6] Further, the refractive index is least for polarization perpendicular to the plane

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bond structures with various charge distributions also enter to an important degree (see later detailed paper).

[*Note added in proof.*—At the Symposium on Liquids and Polyatomic Molecules at the University of Chicago on June 26, Professor Pauling presented new results of *AO* calculations on certain dye spectra in which he has actually used combinations of bond structures with various charge distributions.]

[3] E. Hückel, Zeits. f. Physik **76**, 635, 639 (1932); C. A. Coulson, Proc. Roy. Soc. **A164**, 383 (1938).

[4] L. G. S. Brooker and G. H. Keyes, J. Frank. Inst. **219**, 255 (1935); C. E. K. Mees, J. Opt. Soc. Am. **25**, 81 (1935).

[5] Applications to the problem of molecular refractivities have already been discussed in J. Chem. Phys. **7**, 356 (1939).

[6] H. Waldmann and E. Brandenberger, Zeits. f. Krystallographie **82**, 77 (1932).

of the molecule, as would be expected since *all* $N \rightarrow V$ transitions should be polarized in the plane of the molecule.

IV. Raman Effect Intensities

Again in the Raman effect of a molecule, as is well known, the intensities of the lines depend on the rate of variation of the polarizability during vibration or rotation. In conjugated polyenes, the strong $N \rightarrow V_1$ transition should make a large contribution to the longitudinal polarizability.[1] Since, further, the $N \rightarrow V_1$ intensity is calculated to be very sensitive to the length of the molecule, we may expect the polarizability to vary markedly with such vibrations as cause changes in the over-all length of the molecule (accordion vibrations and so on). Hence, such vibrations should be especially prominent in the Raman spectrum (for suitable exciting wave-lengths). This example illustrates the possibility of getting at least rough information about Raman intensities by means of the type of calculation used in the present work.

The writer is indebted to Professor Edward Teller for first calling to his attention the class of odd polyene dye molecules here considered and for stimulating discussion, and to Dr. Carol A. Rieke for assistance in calculations. Further details on odd-numbered polyene molecules will be given in a later paper.

[*Correction* to Papers VI and VII of present series.[1, 5] In Papers VI (pp. 358–61) and VII (pp. 368–9), it was erroneously stated that the sum of the f values for all transitions arising from a closed shell of m electrons is always just m. Actually it may be somewhat different (distinctly larger than m for outer shells). The writer is indebted to Dr. F. Seitz for calling his attention to this point. This error does not affect the conclusions of VI and VII in any important way. The main effect in VI is to increase the "mean effective frequencies" somewhat, along with the f sums.]

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Remarks on the Calculation of Bond Strength in Methane

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A recomputation has been made of the C−H bond strength in CH_4 by the method of Voge, using more recent data. The premises on which the calculations are based have been examined and it is concluded that the recalculated value (~103 kcal.) is in good agreement with the value of 94.8 kcal. given by Burton when the approximations used in the Voge method are taken into account.

CALCULATIONS of the relative energies of CH_3 and CH_4 were made in 1936 by Voge[1] on the basis of data then available. Since then, some of the data on which the calculations were based have been improved or reinterpreted and also there have been estimates on other bases of the C−H bond strength in CH_4. Voge's data indicate a value of 4.88 volts or 112.6 kcal. for the latter when no allowance is made for zero-point energies of CH_4 and CH_3. On the basis of energies of activation H. S. Taylor and his co-workers[2] have advocated a value of 108 kcal. whereas a computation made by one of us[3] on the basis of photochemical evidence indicates a value of 94.8 kcal. for the energy required to break the first C−H bond in methane. Since such a spread of values is very unsatisfactory in view of the present state of collateral problems it seemed advisable to recalculate Voge's values on the basis of more recent data and to examine the premises on which the calculations were based; the results of such recalculations and examination are here reported.

The significant equation used by Voge for the energy of formation of methane (at the potential energy minimum, not in the ground state) is

$$W(CH_4)-W(C)-4W(H)=W_v(C)+4K(CH_4)+6K(H_2)-3\beta+1/2N_{ss}-5/2N_{s\sigma}-3\sqrt{3}N_{s\sigma}+4N_{\pi\pi}. \quad (1)$$

[1] H. H. Voge, J. Chem. Phys. **4**, 581 (1936).
[2] Trenner, Taylor and Morikawa, J. Chem. Phys. **5**, 203 (1937).
[3] M. Burton, J. Chem. Phys. **6**, 818 (1938).

Like Voge, we use the values $W_v(C)=7.03$; $N_{ss}=2.0$; $N_{s\sigma}=2.3$; and $N_{\pi\pi}=-0.6$ volt. Our other values are different. For the left-hand side, which includes the zero-point energy, we use -16.22 volts, which represents the sum of Burton's value for the heat of formation of CH_4 *not* including the zero-point energy, 346.5 kcal.[4] and Dietz's calculated value of 27.3 kcal. for the zero-point energy.[5]

$K(H_2)$ is the same as the Coulomb energy for the hydrogen molecule and β is the same as the exchange integral for the hydrogen molecule (except for terms of the order of squares of nonorthogonality integrals). Assuming that these values are 10 percent and 90 percent of the Morse function, $M(H_2)$, respectively, and that the C−H distance is 1.09A, as does Voge, we obtain the values $K(H_2)-\frac{1}{2}\beta=0.40$ and $K(CH_4)=-2.65$ volts. Like Voge, we calculate the latter by subtracting $\frac{3}{2}K(H_2)$ from Woods' numerical calculation of the Coulomb energy for CH_4 per bond (i.e., -2.82 volts).[6]

There results for $N_{s\sigma}$ a value of 1.52 volts. This value is now substituted in Voge's equation for the energy of formation of *plane* CH_3 (including the zero-point energy).

$$W(CH_3)-W(C)-3W(H)$$
$$=7.20+3K(CH_4)+3K(H_2)-\tfrac{3}{2}\beta$$
$$-\tfrac{3}{2}N_{s\sigma}-3\sqrt{2}N_{s\sigma}+3N_{\pi\pi}. \quad (2)$$

The use of the term $K(CH_4)$ in this equation is an undesirable but necessary approximation. It involves the implicit assumption that the C−H bond length is not altered on passage from CH_4 to CH_3 and that the Coulomb energy is not affected by the presence of an extra electron. It follows that $K(H_2)-\frac{1}{2}\beta=0.33$ volt. The left-hand side of Eq. (2) then becomes equal to -11.48 volts or 264.9 kcal.

To determine the bond strength in CH_4 we should take into account the zero-point energy of CH_3. Two values which suggest themselves are $\frac{3}{4}$ of that for $CH_4=20.5$ kcal. and $\frac{1}{2}$ that for C_2H_6[5]$=22.1$ kcal. The latter must certainly be a maximum value. On this basis, the heat of formation of CH_3 is 244.4 or 242.8 kcal. and the bond strength in CH_4 is 102.1 or 103.7 kcal.

The values so calculated for the strength of the C−H bond in methane are, of course, only approximations. The assumption that only 10 percent of $M(H_2)$ is Coulombic tends to keep the bond strength down. However, this is perhaps the best of the assumptions made in the calculation.

On the other hand, it seems that the assumption that r_{C-H} is only 1.09A in CH_3 is not justified. It is known that r_{C-H} is 1.12A in free CH.[7] A value of $r_{C-H}>1.09$A in CH_3 would lead to larger values for $3K(H_2)-\frac{3}{2}\beta$ and in turn to smaller bond strengths. An even more pronounced effect is produced by an increase in the Coulomb energy of the C−H bond. An increase over the Coulomb energy in CH_4 seems likely when comparison is made with free CH. In the latter compound, $D_e=3.602$ volts;[7] using Voge's calculations, $K(CH)=-3.28$ volts.

It seems consequently that assumptions that $K(CH_3)-K(CH_4)=0.1$ volt and that $3K(H_2)-\frac{3}{2}\beta$ is 0.1 volt less than that which would correspond to 1.09A are both moderate approximations. Such approximations would lower the bond strength in CH_4 by 0.4 volt (i.e., to ∼94 kcal.)[8]

It may be seen, therefore, that the agreement between the value of 94.8 kcal. (calculated by Burton on the basis of predissociation data) and that of ∼103 kcal. (computed by Voge's method of approximation) is as good as can be expected when we consider the assumptions it was necessary to make in the latter case.

[4] Burton neglected to apply a correction of 0.2 kcal. per carbon atom necessitated by the fact that the data of Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corp., New York), are relative to diamond, not graphite, as the standard state. This correction is here applied. It should be noted that this error cancels out in Burton's bond strength calculations, which are consequently not affected.

[5] V. Dietz, J. Chem. Phys. **3**, 58 (1935).

[6] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932). An undesirable approximation is involved at this point since Woods used $2a_0$ ($=2\times0.5283$A) as the length of the C−H bond.

[7] Cf. G. W. King, J. Chem. Phys. **6**, 378 (1938).

[8] It is also assumed in the quantum-mechanical calculation that the exchange integrals are substantially unchanged. Since the bond length is probably slightly greater in CH_3 than in CH_4 this is not strictly true and consequently the bond strength may be slightly low on this account. However, the presence of the extra electron is adequately accounted for.

The Mechanism of Orientation in *i*-Butyl and *i*-Amyl Bromide Glasses

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The relaxation times of two typical, unassociated polar molecules have been calculated from experimental dispersion data. Both Stokes' law and absolute reaction rate theories have been applied to show that the inner friction constant in the usual Debye relaxation formula must be considered in terms of a mechanism involving higher activation energies than those obtaining in ordinary viscous flow. Hence, the macroscopic viscosity will generally be inadequate as an inner friction constant for relaxation. Slight alterations in the structure of these molecules are found apparently to change their relative orientations and hence energies of interaction. Rotational motion in viscous flow of lesser degree but similar kind to that of relaxation is indicated by the parallelism between the respective energies in *i*-butyl and *i*-amyl bromides. Possible generalizations have been extended to relaxation and flow phenomena in liquid crystals, where effectively the co-existence of phases derived from a single component over a temperature range makes the structure considerations simpler than in the usual case of solutions.

EXPERIMENTS over a range of temperature have provided complete dispersion data at three frequencies for the simple polar molecules of *i*-butyl bromide and *i*-amyl bromide in the vitreous state.[1] These results are considered in terms of the theories of dielectric relaxation, and the mechanisms of molecular motions during rotation and viscous flow. Dielectric loss related to the polar structure of matter has been comprehensively reviewed by Müller.[2]

Debye[3] applied Stokes' expression for the rotation of a sphere in a viscous medium to obtain a relation between the relaxation time, τ, of the molecules, and their radii, a, in which

$$\tau = 4\pi\eta a^3/kT,$$

where η is the inner friction constant, k is the Boltzmann constant, and T is the absolute temperature. This equation is sometimes moderately well obeyed for dilute solutions of polar molecules, where η is taken as the viscosity of the solvent, but must be modified when there is pronounced intermolecular action, such as obtains in a pure polar substance, as Debye[4] and others have recognized. Then, η can no longer be a simple macroscopic viscosity, and we shall consider the relaxation time in terms of molecular processes. For comparison with this latter treatment, however, the classical relaxation times of the bromides have been calculated. By a graphical extrapolation from the data reported, ϵ_1, the dielectric constant at zero frequency is evaluated, and ϵ_0, that at infinite frequency, is, with sufficient accuracy, given by the low temperature solid value, or the square of the refractive index. The calculation of τ then follows from Debye's[5] equation

$$\omega\tau = \frac{\epsilon_0+2}{\epsilon_1+2}\left[\tfrac{1}{2}\{y+(4+y^2)^{\frac{1}{2}}\}\right]^{\frac{1}{2}},$$

where $\omega = 2\pi f$, f = frequency in cycles per second, $y = (\epsilon_1-\epsilon_0)/(\epsilon_1+\epsilon_0)$. The relaxation times, in each case at a temperature corresponding to maximum dispersion for 50 kc., are:

i-butyl bromide, $\tau = 0.9\times10^{-6}$ sec. at 118.6°K;
i-amyl bromide, $\tau = 1.2\times10^{-6}$ sec. at 131.1°K.

Rough estimates of kinetic theory radii from Sutherland's constant data (Landolt-Börnstein's "*Tabellen*") may be used to calculate η values: *i*-butyl bromide, for $a^3 = 16.64\times10^{-24}$ cm^3, $\eta = 0.68\times10^2$ poise at 118.6°K; *i*-amyl bromide, for $a^3 = 20.91\times10^{-24}$ cm^3, $\eta = 0.79\times10^2$ poise at 131.1°K. Lillie[6] showed that there is no discontinuity in η at the vitrification point, while Eyring[7] has theoretically justified a linear relation between ln η and $1/T$ which permits extrapolation of the viscosity data of Thorpe and

[1] Baker and Smyth, J. Am. Chem. Soc. 61 (1939).
[2] Müller, *Ergebnisse der Exakten Naturwissenschaften* (Julius Springer, Berlin, 1938), Vol. XVII, pp. 164–228.
[3] Debye, *Polar Molecules* (Chemical Catalog Co., Inc., New York, 1929), p. 85.
[4] P. Debye and W. Ramm, Ann. d. Physik **28**, 28 (1937).
[5] Reference 3, p. 94.
[6] H. R. Lillie, J. Am. Ceram. Soc. **16**, 619 (1933).
[7] H. Eyring, J. Chem. Phys. **4**, 283 (1936). See also, E. N. Andrade, Nature **125**, 580 (1930); S. E. Sheppard, J. Rheology **1**, 349 (1930).

Rodger[8] for *i*-butyl bromide to the temperature at which the relaxation time was measured. Although the value thus obtained, $\eta=0.90$ poise at 118.6°K, is very approximate, it demonstrates, by being 100 times too small, the inadequacy of the simple macroscopic viscosity in specifying the rotational hindrance in a pure polar medium. Of course, the linear extrapolation of the liquid viscosity values into the glass region is made uncertain by the possibility that the mechanism of viscous flow has changed, but even this would probably not account for the discrepancy between the extrapolated and calculated values.

A method for considering the relaxation phenomenon as a molecular process has been suggested by Eyring,[7, 9] and further developed by Frank,[10], who made calculations for ice, some solid solutions in paraffin wax, and for a composite commercial insulator, Permitol. We propose to extend this treatment to the simple, homogeneous bromide glasses. The quantal basis for the theory of absolute reaction-rates[11] gives an expression for the rate at which an activated complex formed at the top of a potential hump decomposes to give the products. In the case of a unimolecular reaction, this is effectively the surmounting of a potential barrier, which may readily be considered as that imposed by its neighbors to restrict the rotation of a given molecule. The standard Arrhenius form for a unimolecular reaction will yield an activation energy for the process, since $\log \tau$ is found to be practically a linear function of T, and $1/\tau=k'=Ce^{-A/RT}$, where $k'=$specific reaction rate, $A=$activation energy, $C=$"steric factor," later to be explicitly defined. The τ to be used above is most accurately found by regarding it as the mean relaxation time for the temperature of maximum dielectric loss. That is, considering the decay of orientation as an exponential function of time, Debye[5] has derived the relations

$$\epsilon'=\epsilon_0+\frac{\epsilon_1-\epsilon_0}{1+x^2},$$

$$\epsilon''=\frac{\epsilon_1-\epsilon_0}{1+x^2}x,$$

in which the quantities preserve their already defined meanings, and

$$x=\frac{\epsilon_1+2}{\epsilon_0+2}\omega\tau,$$

while ϵ'' is the loss component of the dielectric constant as indicated by the equation $\epsilon=\epsilon'-i\epsilon''$. Clearly, ϵ'' reaches a maximum when $x=1$, and the temperatures of these maxima are obtained from the experimental work quite independently of the absolute values of ϵ'', since the graphs of ϵ'' against temperature are symmetrical.[1] We now find that

$$-d \ln \tau/dT=A/RT^2,$$

or, since $\omega=2\pi f$, and $\tau=1/\omega$ at the critical frequency, then

$$d \ln f/dT=A/RT^2.$$

Thus, A/R values result from the slope of the straight line obtained by plotting $\ln f$ against $1/T$, where T is the temperature of maximum ϵ'' for the given frequency f. Further, a mean T of ϵ''_{max} may be found, and from it a mean f, which may be then used to calculate the specific rate, a mean $1/\tau$, from

$$1/\tau=\frac{\epsilon_1+2}{\epsilon_0+2}\cdot 2\pi f.$$

The fundamental equation $k'=\kappa kT/he^{-\Delta F^{\mp}/RT}$, where $\kappa=$transmission coefficient, taken as 1, $k=$Boltzmann's constant, $h=$Planck's constant, and $\Delta F^{\mp}=$free energy of activation, may now be used to calculate $\Delta F^{\mp}$. It may also be rewritten as

$$k'=\kappa kT/he^{\Delta S^{\mp}/R}e^{-\Delta H^{\mp}/RT},$$

where $\Delta S^{\mp}$ is the activation entropy, and $\Delta H^{\mp}$ is the heat of activation taken as the activation energy A for the rotation process. The factor C thus includes the terms $\kappa kT/he^{\Delta S^{\mp}/R}$. The mechanism of the rotation of vitreous *i*-butyl and *i*-amyl bromides may now be interpreted from the results given in Table I.

It is evident from the large entropy terms that many molecules surrounding a given one able to orient in the field must cooperate in permitting its orientation. Probably, they undergo, by thermal fluctuations, slight rearrangements, a very definite combination of these

[8] Landolt-Börnstein, *Tabellen* (Julius Springer, Berlin, 1935), 5th ed., Vol. I.
[9] A. E. Stearn and H. Eyring, J. Chem. Phys. **5**, 113 (1937).
[10] F. C. Frank, Trans. Faraday Soc. **32**, 1634 (1936).
[11] H. Eyring, Chem. Rev. **17**, 65 (1935).

TABLE I.

	T_{MEAN} °K	f_{MEAN}	A (CAL./MOLE)	C	$\Delta F^{\mp}$ (CAL./MOLE)	$\Delta S^{\mp}$ (E.U./MOLE)
i-Butyl bromide	115.6	5.6×10^{3}	23,108	7.86×10^{48}	3796	167.1
i-Amyl bromide	128.0	5.0×10^{3}	18,007	5.21×10^{35}	4425	106.1

being necessary for a single molecule to be able to rotate. In the liquid state, this entropy factor is small. Hence, this direct evidence explains the great difference in solid and liquid values of properties involving rotational motion, as viscosity and diffusion. The activation energy for viscous flow in glass or even in steel may not differ greatly from that in the molten state, but high entropy terms will vastly retard the processes concerned in the solid state. These results should also be applied to the mechanical properties of rigid mixtures, such as plastics and resins, where elasticity or resiliency as well as dielectric properties may depend on the effect of cross linkages and foreign ingredients upon the orientation entropies of the molecules.

Although the additional methylene group in *i*-amyl bromide somewhat dilutes the dipoles, this alone is not sufficient to account either for the lower activation energy for rotation, 18 kcal., or for the reduced maximum dielectric constant, 12.3, of the larger molecule as compared to values of 23 kcal. and 17.3, respectively, for *i*-butyl bromide. However, this difference would be expected if the elongated pear shape of the *i*-amyl as contrasted to the compressed pear shape of the *i*-butyl compound had introduced sufficient anisotropy to make the former molecule rotate preferably only about its long axis. Independent evidence that this slight structural change has indeed produced such an effect, and, conversely, independent support from the dielectric measurements for the rotating couple concept of viscous flow[7, 12] arise from examination of the activation energies of viscosity for these compounds. These energies, given in Table II, were calculated from the data of Thorpe and Rodger.[8] According to the Eyring theory of viscosity, the flow process occurs in a fashion requiring the least use of extra volume, for to make a hole the size of a molecule requires the energy of vaporization of the molecule. For nearly spherical, or quite symmetrical molecules, no preferred orientations of the molecules forming the rotating couple are possible, and the ratio of the energy of vaporization to the activation energy for viscous flow, $\Delta E_{vap}/\Delta E_{vis}$, is generally found to be about 3.[12] However, rod-like molecules will align along their long axes, and then the ratio $\Delta E_{vap}/\Delta E_{vis}$ is 4 or even larger. If, then, *i*-amyl bromide is tending to behave as an extended molecule, while the *i*-butyl bromide is more isotropic, the ΔE_{vis} values should be in the same order as, although of quite different magnitudes from, the activation energies for orientation. This is confirmed by Table II, in which the activation energy for rotation, A, is again given, and, further, the $\Delta E_{vap}/\Delta E_{vis}$ ratio of 3.5 for *i*-butyl bromide differs from the value 4.3 for the longer *i*-amyl bromide. Thus, the interrelation of the previously unconnected mechanisms of the kinetic processes of dielectric relaxation and viscous flow is seen to be consistent with the structure of the molecules. Such a method of deciding about the mode of orientation processes should prove general.

It has been noted in a discussion of the swarm theory of liquid crystals[13] that the relaxation time of para-azoxyanisole groups, as measured by the region of maximum dispersion for a given frequency, varies rapidly with temperature. However, the experimental viscosity shows a normal slow change with temperature. It is also shown from optical studies that the groups are altered in size only very gradually with temperature. These relaxation time-viscosity phenomena, anomalous in the classical theory, would seem to be explained by the previous evidence that the process of viscous flow requires an activation energy which is only a fraction of that required for rotation of the particles orienting in a field.

TABLE II.

	ΔE_{VIS} (CAL./MOLE)	A (CAL./MOLE)	$\Delta E_{VAP}/\Delta E_{VIS}$ (CAL./MOLE)
i-Butyl bromide	1990	23,108	3.5
i-Amyl bromide	1759	18,007	4.3

[12] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).

[13] L. Ornstein and W. Kast, Trans. Faraday Soc. **29**, 931 (1933).

Hence, the temperature coefficient of the relaxation rate would exceed that of the viscosity change, as observed.

The viscosity of liquid crystalline systems is also found to show a maximum with increasing temperature in the anisotropic region[14] instead of the uniform decrease found with normal liquids. Too, the Hagen-Poiseuille law is not obeyed, and liquid crystal mixtures appear to have a disproportionately high viscosity for low pressures.[14] Ostwald has termed this a "structure viscosity" effect, without further explanation. The structure sensitivity is quantitatively illustrated in the bromides discussed above. If the difference of a methylene group so alters the flow orientation of the molecules, as here indicated, it is understandable that the liquid crystalline groups may, by relatively small changes in shape, engage in a variety of flow processes. These changes in shape may be effected by temperature. Thus, at certain temperatures, the activation energy for viscous flow may change so much as to produce temporarily an apparent increase of viscosity over that found for a lower temperature. Also, the local group orientation will be influenced by the rate of flow through a capillary, and, again, the activation energies and hence apparent viscosities as well as actual flow mechanism may change as they would not do in the normal case of the passage through a capillary of a liquid whose flow units are of molecular size too small to be oriented by the streaming through the tube. Further, as expected, it is found that the plot of $\ln \eta$ against $1/T$ for a liquid crystalline substance has not only a different slope from that of the isotropic liquid, but often deviates from linearity in the region where the swarms are changing, presumably in shape and size. This is again possible evidence for a varying activation energy in the absolute reaction rate theory of viscosity.[7] It may be concluded that at least qualitatively this theory is applicable to systems exhibiting viscosities often considered anomalous. There is probably, of course, the additional factor that other terms besides the energy exponential in the specific rate expression for viscosity[7, 12] change in the cases considered above, but the dielectric relaxation results have shown how sensitive potentials involving rotational interaction are to the shape of the interacting units.

A somewhat different theoretical approach to the viscosity of anisotropic liquids, in which the rotational motion is represented in terms of the center of mass and the turning moment has been offered.[15] It has not been applied to the effects here discussed. Bingham[16] also suggested, without further detail, that a new molecular arrangement was probably formed at the clarifying point of a crystalline liquid. The viscosity-temperature relation of *p*-azoxyanisole resembles significantly that for liquid sulfur[17] in the region of its anomaly. A change of structure has been proposed to explain the sulfur behavior.[13]

Oncley and Williams[18] have noted the deficiencies of the macroscopic viscosity in relaxation time calculations in reporting that the measured viscosity of a solution might be increased a thousand-fold without changing significantly the value of the inner friction constant in the Debye formula. They varied the viscosity by using mixtures of hydrocarbon oils or waxy compounds. On the present scheme of regarding orientation as the surmounting by the polar solute molecules of potential barriers created, at least in moderately dilute solutions, chiefly by the solvent molecules, lengthening of the solvent molecules would presumably not alter the average environment of the solute. Hence, just the results of Oncley and Williams would be expected, as in the rotation of the polar molecule in the field in contrast to the viscous flow of the solution, the solvent molecules need not themselves rotate.

[14] Wo. Ostwald, Trans. Faraday Soc. **29**, 1002 (1933).

[15] R. O. Herzog and H. Kuder, Trans. Faraday Soc. **29**, 1006 (1933).

[16] E. C. Bingham, *Fluidity and Plasticity* (McGraw-Hill Book Co., Inc., New York, 1922), p. 210.

[17] L. Rotinjanz, Zeits. f. physik. Chemie **62**, 609 (1908).

[18] J. L. Oncley and J. W. Williams, Phys. Rev. **43**, 341 (1933).

Critical Behavior of Solid Solutions in the Order-Disorder Transformation

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A discussion of critical phenomena in the order-disorder transformation from the standpoint of the theories of Bethe and Kirkwood is presented. A comparison of the two theories is undertaken, and the best values of the transition temperatures and heat capacity anomalies, ΔC_v, for the simple cubic and body-centered cubic lattices are tabulated. The influence of anomalies in the coefficients of expansion and compressibility on the anomaly in the heat capacity C_p is investigated.

THE theory of order and disorder in solid solutions originally formulated by Bragg and Williams[1] has been elaborated on the basis of a more detailed crystalline model by Bethe[2] and by Kirkwood.[3] It is the purpose of the present article to compare the methods of Bethe and Kirkwood particularly in the results they give at the order-disorder transition temperature. For this purpose, a new formulation of the Bethe method is employed, which has the advantage of yielding closed expressions for the thermodynamic functions of the crystal. The new formulation will be described in detail in a later article. The results of the two methods were previously believed to differ significantly only in the magnitude of the heat capacity anomaly at the critical temperature.[4] We shall show that this discrepancy is removed by a more precise use of the method of moments at the critical temperature. The anomaly in C_v for a body-centered cubic crystal remains about one-fourth the observed anomaly in C_p for β-brass as measured by Sykes and Moser. Eisenschitz[5] has suggested that this difference is due to a real anomaly in C_p-C_v associated with anomalies in the coefficients of expansion and compressibility of the crystal. We shall discuss the possibilities of this view.

We take as our model a binary solid solution consisting of N_0 atoms of type 1 and N_0 atoms of type 2, the crystal being built up of two interpenetrating simple lattices A and B of N_0 sites each, occupied by a total number of atoms N, equal to $2N_0$. We denote by N_1^A and N_1^B the numbers of atoms of type 1 on the respective lattices and by x_1^A and x_1^B the atom fractions of component 1 on the two lattices. The long range order of the crystal is defined in the usual manner.

$$s=x_1^A-x_1^B. \tag{1}$$

A configuration of the crystal may be uniquely specified by a set of numbers $\xi_1, \cdots \xi_{N0}, \eta_1, \cdots \eta_{N0}$ where ξ_a states the number of atoms of type 1 in site a of lattice A and η_b the number of atoms of type 1 in site b of lattice B. Each variable ξ_a and η_b has a domain of two values, zero and unity. The configurational partition function of the crystal for a fixed degree of long range order may be written as follows,

$$f=\sum_{\substack{\xi_1,\cdots\xi_{N_0}=0 \\ \Sigma\xi_a=N_1^A}}^{1}\ \sum_{\substack{\eta_1,\cdots\eta_{N_0}=0 \\ \Sigma\eta_b=N_1^B}}^{1} \exp\left(-2\alpha\sum_{a,\,b=1}^{N_0}\lambda_{ab}\xi_a\eta_b\right), \tag{2}$$

$$N_1^A=(N/4)(1+s), \quad N_1^B=(N/4)(1-s),$$

$$\alpha=V/kT, \qquad V=(V_{11}+V_{22})/2-V_{12},$$

where V_{11}, V_{22}, and V_{12} are the mutual potential energies of the indicated types of nearest neighbor pair and the zero of energy is that of the completely ordered crystal at absolute zero. The neighbor matrix λ_{ab} is characterized by the fact that λ_{ab} is unity if sites a and b are nearest neighbors and zero otherwise. Evidently we may write

$$\sum_{a=1}^{N_0}\lambda_{ab}=\sum_{b=1}^{N_0}\lambda_{ab}=z, \tag{3}$$

where z is the number of nearest neighbors of any site. If it is desired to take account of interactions of higher order than those of nearest

[1] Bragg and Williams, Proc. Roy. Soc. London **A145**, 699 (1934); **151**, 540 (1935); **152**, 231 (1935).
[2] Bethe, Proc. Roy. Soc. London **A150**, 552 (1935).
[3] Kirkwood, J. Chem. Phys. **6**, 70 (1938).
[4] See Nix and Shockley, Rev. Mod. Phys. **10**, 1 (1938).
[5] Eisenschitz, Proc. Roy. Soc. London **168A**, 546 (1938).

neighbors, the generalization of the neighbor matrix is obvious. For simplicity we shall assume only nearest neighbor interaction here. Since the partition function f reduces to the total number of configurations consistent with the specified degree of long range order, for vanishing α, we may define a function $G(\alpha, s^2)$, vanishing for α equal to zero, by the relation

$$f=\left(\frac{1+s}{2}\right)^{-N(1+s)/2}\left(\frac{1-s}{2}\right)^{-N(1-s)/2}e^{NzG(\alpha, s^2)}, \quad (4)$$

where the first factor is equal to the total number of configurations for fixed s. From the form of the partition function (2), it is obvious that G is an even function of s and therefore a single valued function of s^2. The configurational free energy, equal to $-kT\log f$ may be expressed as follows,

$$-F/NkT=-\left(\frac{1+s}{2}\right)\log\left(\frac{1+s}{2}\right)-\left(\frac{1-s}{2}\right)\log\left(\frac{1-s}{2}\right)+zG(\alpha, s^2). \quad (5)$$

Determination of the equilibrium degree of long range order by minimization of the free energy at constant α leads to the condition

$$\log\frac{1+s}{1-s}=4zs\frac{\partial G}{\partial(s^2)}. \quad (6)$$

Assuming $G(\alpha, s^2)$ to be an analytic function of s^2, we may write

$$G(\alpha, s^2)=G_0(\alpha)+s^2G_1(\alpha)+s^4G_2(\alpha)+\cdots. \quad (7)$$

For a phase change of the second kind, Eq. (6) has no real solutions other than $s=0$ for values of α less than a critical value satisfying the equation,

$$2zG_1(\alpha_c)=1 \quad (8)$$

with a critical temperature T_c equal to $V/k\alpha_c$. For values of α greater than α_c, there exist two nonvanishing real solutions, $\pm s$, of minimum free energy, yielding a unique equilibrium value of s^2. The approximate forms of $G(\alpha, s^2)$ which we shall discuss satisfy these conditions, although it has not been rigorously proved that the exact form does.

The heat capacities C_v^+ and C_v^- just above and just below the critical temperature have the form

$$\frac{C_v^- - C_v^+}{Nk}=\frac{6[z\alpha_c dG_1/d\alpha]^2}{1-12zG_2(\alpha_c)},$$
$$C_v^+/Nk=z\alpha_c^2 d^2G_0/d\alpha^2. \quad (9)$$

For the calculation of the discontinuity in the heat capacity at the critical temperature a knowledge of $G_1(\alpha)$ and $G_2(\alpha)$ is sufficient.[5] However, since ΔC_v is extremely sensitive to the value of $G_2(\alpha_c)$, the latter must be known with accuracy.

We may now discuss the forms of $G(\alpha, s^2)$ provided by the several theories of order and disorder. In a later paper, we shall find for the Bethe theory

$$G(\alpha, s^2)=-\left(\frac{1+s}{4}\right)\log\left[\frac{2(y+s)}{(y+1)(1+s)}\right]-\left(\frac{1-s}{4}\right)\log\left[\frac{2(y-s)}{(y+1)(1-s)}\right], \quad (10)$$
$$y=[s^2+(1-s^2)e^{2\alpha}]^{\frac{1}{2}}.$$

Expansion in powers of s^2 yields

$$G_0(\alpha)=(\tfrac{1}{2})\log\left(\frac{1+e^{-\alpha}}{2}\right);\quad G_1(\alpha)=\frac{1-e^{-\alpha}}{4}$$
$$G_2(\alpha)=\frac{1}{24}[1-\tfrac{3}{2}e^{-\alpha}+\tfrac{1}{2}e^{-3\alpha}]. \quad (11)$$

From Eqs. (8) and (11), one obtains for the critical value of α

$$\alpha_c=\log[z/(z-2)]. \quad (12)$$

The discontinuity of the heat capacity at the critical temperature follows from Eqs. (9), (11), and (12).

$$\frac{\Delta C_v}{Nk}=\frac{3z^2}{8}\frac{z-1}{z-2}\left[\log\left(\frac{z}{z-2}\right)\right]^2. \quad (13)$$

For a simple cubic lattice, $z=6$, $\Delta C_v/Nk$ has the value 1.78 and for a body-centered lattice, $z=8$, the value 1.70. The Bragg and Williams value is 1.50.

[5] See Borelius, Ann. d. Physik **20**, 57 (1934).

TABLE I.

APPROXIMATION	$z=6,\ \zeta=3$		$z=8,\ \zeta=11$	
	kT_c/V	$\Delta C_v/Nk$	kT_c/V	$\Delta C_v/Nk$
0	3.00	1.50	4.00	1.50
1	2.57	1.75	3.55	1.69
2	2.49	1.78	3.49	1.70
3	2.44	1.86	3.41	1.81
B_1	2.47	1.78	3.48	1.70
B_2	2.37	1.94		

In the Kirkwood theory,* the exact configurational partition function is expanded in powers of α, leading to the following expression for $G(\alpha, s^2)$

$$G(\alpha, s^2)=\sum_{n=1}^{\infty}(-1)^n\alpha^n\lambda_n/(Nz)(n!), \qquad (14)$$

where the Thiele semi-invariants λ_n are related to the moments M_n of the sum

$$2\sum_{a,\ b=1}^{N_0}\lambda_{ab}\eta_b\xi_a$$

in the following manner

$$\sum_{m=1}^{n}\binom{n-1}{m-1}\lambda_m M_{n-m}=M_n; \quad n=1, 2\cdots. \qquad (15)$$

The moment M_n is an *a priori* average of the sum,

$$\left(2\sum_{a,\ b}\lambda_{ab}\xi_a\eta_b\right)^n$$

over all crystalline configurations of fixed s. The method of calculation has been described by Kirkwood.[3] The first four moments have been calculated and are presented below

$$\begin{aligned}
&\lambda_1/Nz=(1-s^2)/4,\\
&\lambda_2/Nz=(1-s^2)^2/8,\\
&\lambda_3/Nz=-s^2(1-s^2)^2/4,\\
&\lambda_4/Nz=(1-s^2)^2[2(1-3s^2)^2+3\zeta(1-s^2)^2]/16,\\
&\zeta=(1/z)[\sum_{a'=1\neq a}^{N_0}z_{aa'}{}^2-z^2],
\end{aligned} \qquad (16)$$

where $z_{a'a}$ is the number of common neighbors on lattice B of the pair of sites a' and a on lattice A. For a simple cubic lattice ζ is equal to 3 and for a body-centered lattice 11. We remark that characteristics of the crystal structure other than the coordination number z begin to appear at the fourth moment. Expansion of the right-hand side of Eq. (10) in powers of α shows that the $G(\alpha, s^2)$ of the Bethe theory is accurate to the third moment but is incorrect in the fourth moment.

For the calculation of the discontinuity of the heat capacity at the critical temperature, we expand the $G(\alpha, s^2)$ of Eqs. (14) and (16) in powers of s^2 with the result,

$$\begin{aligned}
G_0(\alpha)&=-\alpha/4+\alpha^2/16+(2+3\zeta)\alpha^4/384+\cdots\\
G_1(\alpha)&=\alpha/4-\alpha^2/8+\alpha^3/24\\
&\qquad -(4+3\zeta)\alpha^4/96+\cdots\\
G_2(\alpha)&=\alpha^2/16-\alpha^3/12+(22+9\zeta)\alpha^4/192+\cdots.
\end{aligned} \qquad (17)$$

With the aid of Eq. (8) and the expansion (17) for $G_1(\alpha)$, the critical value of α may be expanded in powers of $1/z$.

$$\alpha_c=(2/z)[1+1/z+4/3z^2+(3+\zeta)/z^3+\cdots]. \qquad (18)$$

Use of the series (17) and (18) in Eq. (9) and expansion in powers of $1/z$ yields for the heat capacity discontinuity

$$\Delta C_v/Nk=(3/2)[1+1/z+2/3z^2+3(1+\zeta)/z^3+\cdots]. \qquad (19)$$

To obtain terms of order z^{-4} in the expansions (18) and (19), the fifth moment is required. The critical temperatures and the heat capacity anomalies computed by Eqs. (18) and (19) and by Bethe's first (B_1) and second (B_2) approximations are presented in Table I, for the simple cubic and the body-centered cubic lattices. The Bethe first approximation, valid to the third moment in the energy, does not differ significantly from the Kirkwood second approximation in which terms including the third moment are retained. The Bethe second approximation deviates somewhat from the Kirkwood third approximation in which the fourth moment is retained. It has not been verified whether the Bethe second approximation, which is extremely tedious to analyze, is valid to the fourth moment or not. The values of kT_c/V and $\Delta C_v/Nk$, presented in

* For convenience, certain changes in notation from reference 3 have been made in the present article. The present α differs from the α of reference 3 by a factor $2/Z$.

Table II, appear to represent the best approximations obtainable from the assembled calculations. In Kirkwood's original first approximation, based on the second moment of energy, the values 2.37 and 4.1 were obtained for kT_c/V and $\Delta C_v/Nk$. These values are obtained if the linear and quadratic terms of the expansions (17) are substituted into Eqs. (8) and (9) without the subsequent expansion in powers of $1/z$. Due to the extreme sensitivity of the right-hand side of Eq. (9) to the value of $G_2(\alpha_c)$, this procedure leads to the abnormally high value 4.1 for the heat capacity anomaly. The expansion in powers of $1/z$ employed here avoids this difficulty. Exact values of the coefficients in the series (18) and (19) to terms of degree one less than the order of the last moment retained are provided by the method.

Eisenschitz[5] has raised the question of the reality of the heat capacity anomaly at the transition temperature. It is of course true that for a finite lattice, the partition function is an analytic function of the reciprocal temperature and that on the basis of statistical mechanics the mean energy and heat capacity are, strictly speaking, continuous functions of the temperature. However, as Eisenschitz has shown, the derivative $-dC_v/dT$ is of the order $N^{\frac{1}{2}}$ at the critical temperature, where N is the total number of atoms. In any macro-crystal N is so large that a physical discontinuity would be observed, since the mathematical continuity would be obscured not only by the practical limit of precision of measurement but also by the theoretical limit of precision imposed by the fluctuation theory of statistical mechanics on the measurement of any thermodynamic function. However, Eisenschitz goes a step further, maintaining that the effective thermodynamic unit of a crystal is a molecular domain composed of approximately 10^4 atoms, small enough to reveal the mathematical continuity of C_v. His argument for such an assumption does not seem adequate to us, nor does the experimental evidence for a finite slope in the heat capacity curve of β-brass at the transition point seem conclusive enough to give empirical justification for the assumption. Eisenschitz points out that exactly at the critical temperature, it is no longer correct to approximate the complete partition function

$$\sum_{s=-1}^{+1} f(s)$$

by its maximum term, as we have done. On the basis of the Bragg and Williams approximation (our zero approximation) he computes a value 0.6 for C_v/R. Because of an error in his transformation of the sum over s to an integral, this value should properly be 0.8. For an infinite lattice, this value has no significance since C_v is not a single valued function of the temperature at T_c. We also believe that it has no physical significance for a finite lattice of macroscopic dimensions, since it can easily be shown that at a temperature satisfying the relation $|T-T_c|/T_c \geqslant N^{-\frac{1}{4}}$ the error in approximating the partition function,

$$\sum_{s=-1}^{+1} f(s),$$

by its maximum term is of the order $N^{-\frac{1}{4}}$. Unless the Eisenschitz domains are admitted, these points become trivial. It is of course true that domains of the type encountered in ferromagnetism enter into the formation of superlattices, but they are of essentially macroscopic dimensions and contain a sufficient number of atoms to give the observed physical discontinuities. Were the independent domains as small as Eisenschitz maintains, sharp superlattice lines in the x-ray reflections from an ordered crystal would not be observed.

There is a large discrepancy between the observed anomaly in C_p as given by the data of Sykes and Moser for β-brass and the calculated anomaly in C_v for a body-centered cubic lattice. The discrepancy is doubtless due in part to deficiencies in the theory, such as the neglect of the coupling between lattice vibrations and configuration and the simplifying assumptions concerning the atomic interactions, but seems far too large to account for on this basis alone. From thermodynamics we know that

TABLE II.

LATTICE	kT_c/V	$\Delta C_v/Nk$
Simple Cubic	2.4	1.9
Body-Centered Cubic	3.4	1.8

$$C_p-C_v=\beta^2vT/\kappa$$
$$\beta=-\frac{1}{v}\left(\frac{dv}{dT}\right)_p;\quad \kappa=-\frac{1}{v}\left(\frac{dv}{dp}\right)_T, \tag{20}$$

where β and κ are the coefficients of expansion and compressibility. Eisenschitz has made the important suggestion that there is a large anomaly in C_p-C_v at the critical temperature due to the dependence of the interaction energy of neighbors, V, on the expansion of the lattice. He has undertaken the calculation of C_p in zero approximation without explicit use of Eq. (20), using the partition function at constant pressure. Reasonable assumptions concerning the dependence of V on the volume of the crystal lead to an anomaly in C_p for β-brass of the experimental magnitude. Eisenschitz's essential results can perhaps be obtained in a more simple fashion by the use of thermodynamics and our partition function (4). From Eq. (5), we easily obtain the following equation of state,

$$p=p'+\gamma\bar{E}/v$$
$$\gamma=-(v/V)(dV/dv) \tag{21}$$

where $\bar{E}$ is the mean configurational energy, v is the volume and p' is the pressure due to nonconfigurational contributions to the free energy, and p is the total pressure. We remark that p, $\bar{E}$, and p' as well as the derivatives of p' must be continuous functions of the temperature. Moreover $\bar{E}$ depends explicity only on α and s^2 and the equilibrium value of s^2 is a function of α alone. Therefore $\bar{E}$ depends implicitly on the volume only through the variable α. Using these facts, we may compute the anomalies in the coefficients of expansion and compressibility from the equation of state,

$$\Delta\beta=(\gamma_0\kappa_+\Delta C_v/v)\frac{1+\gamma_0\beta_+T_c}{1-\gamma_0^2\kappa_+T_c\Delta C_v/v},$$
$$\Delta\kappa=\frac{\gamma_0^2\kappa_+^2T_c\Delta C_v/v}{1-\gamma_0^2\kappa_+T_c\Delta C_v/v}, \tag{22}$$

where β_+ and κ_+ are the coefficients of expansion and compressibility just above the critical temperature and γ_0 is the value of γ at the critical temperature. In a similar manner, the anomaly ΔC_p may be calculated from Eqs. (20) and (21)

$$\Delta C_p=\frac{(1+\gamma_0\beta_+T_c)^2}{1-\gamma_0^2\kappa_+T_c\Delta C_v/v}\Delta C_v. \tag{23}$$

It is interesting to apply Eq. (23) to the case of β-brass. The critical temperature is 740°K and $\Delta C_p/R$ is approximately 8 according to the measurements of Sykes and Moser. Approximating β_+ and κ_+ by the mean coefficients of copper and zinc and using the theoretical value 1.8 for $\Delta C_v/R$, we find that the experimental value of ΔC_p corresponds to a value of γ_0 of about 2.3. While no objection can be made to the magnitude of this value, it is difficult to obtain a good theoretical check on γ. Eisenschitz represents γ as a function of the volume by a two-constant equation, which we shall not discuss here.

While Eisenschitz's proposal doubtless disposes of an important part of the discrepancy between theory and experiment, the necessity of introducing empirical constants in comparison of theory and experiment may well obscure real discrepancies of smaller magnitude. Since $\Delta C_v/R$ is the only quantity predicted by the theory involving no parameters to be determined from experiment, it would be extremely desirable to have experimental values of this quantity itself. Measurements of the anomalies of the coefficients of expansion and compressibility as well as of C_p would provide the necessary information for an adequate test of the theory. Data[6] at present available are inadequate for a quantitative test.

[6] Grube, Schönmann, Vaupel and Weber, Zeit. f. Anorg. u. Allgem. Chemie **201**, 41 (1931).
Matsuda, Sci. Rep. Tohoku Imp. Univ. **11**, 223 (1922).

Corresponding States for Perfect Liquids

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On the basis of certain assumptions concerning the properties of the molecules, and by using classical statistics, the van der Waals theory of corresponding states is derived. No mathematical approximations are involved. Argon, krypton and xenon, which conform closely to the assumptions, show the expected correspondence in behavior and are taken as standards. The name *perfect liquid* is suggested for this behavior. In a second part, the deviations from perfection are discussed for a wide variety of substances. Particularly considered are heat capacities and entropies of vaporization which should be compared at points where the vapor to liquid volume ratio has the same value. The observed deviations are explained in a general way.

INTRODUCTION

THE idea of corresponding states arose from the equation of state proposed by van der Waals and was suggested by him in 1873. The theory of corresponding states is of course more general than the equation and holds that in terms of reduced temperatures (T/T_{crit}), volumes, etc., the behavior of all substances should be the same. At that time the available knowledge of the properties of individual molecules was insufficient for a really satisfactory theoretical derivation in these terms or to indicate what substances should follow this theory. Recently such knowledge has become available, particularly due to the work of London and others on the nature of van der Waals forces. The following is a derivation of the theory of corresponding states on the basis of assumptions compatible with the new knowledge of molecular forces.

Recently de Boer and Michels[1] have discussed the theory of corresponding states with respect to gas imperfection, but the writer is not aware of any recent consideration of the liquid from this point of view.

In addition to the theory of corresponding states, in terms of the critical point, there is Trouton's rule and its various modifications, most notably that of Hildebrand.[2] While our derivation will lead to the van der Waals theory of corresponding states, it will be shown that for certain common groups of substances it becomes equivalent to the Hildebrand rule.

On the basis of modern molecular knowledge Eyring and co-workers,[3] Lennard-Jones and Devonshire,[4] Mayer and co-workers,[5] and Rice[6] have recently presented theoretical treatments of liquids which have been successful in accounting for the properties of that state. The aim of these investigations was somewhat different from that of the present one. While we shall hope only to establish theoretically the proper basis for comparison of liquid properties, these investigators attempted to calculate the properties themselves. On the other hand, we shall avoid some of the approximations which have been made in the more penetrating discussions.

After completing in Part I our derivation of the law of corresponding states and comparing the data for a group of substances fitting the assumptions, a brief discussion will be given in Part II of the various deviation from the law. Professor J. H. Hildebrand[7] has recently considered the deviations of a somewhat different group of substances from this point of view.

PART I

Perfect liquids

The following assumptions must be made for our theoretical derivation. First, classical sta-

[1] J. deBoer and A. Michels, Physica **5**, 945 (1938).
[2] J. H. Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915); **40**, 45 (1918).
[3] H. Eyring and Hirshfelder, J. Phys. Chem. **41**, 249 (1937); Newton and H. Eyring, Trans. Faraday Soc. **33**, 73, 80 (1936).
[4] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. London **A165**, 1 (1938).
[5] J. E. Mayer, J. Chem. Phys. **5**, 63 (1937); J. E. Mayer and P. G. Ackerman, *ibid.* **5**, 74 (1937); J. E. Mayer and S. F. Harrison, *ibid.* **6**, 87, 101 (1938).
[6] O. K. Rice, J. Chem. Phys. **5**, 353 (1937) and earlier papers.
[7] J. H. Hildebrand, J. Chem. Phys. **7**, 233 (1939).

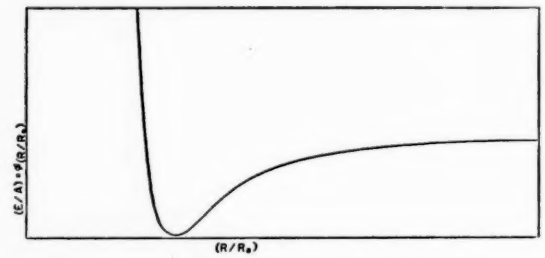

FIG. 1. The approximate curve of the function φ.

tistical mechanics will be used. As an example, this assumption for a harmonically vibrating solid gives the Dulong and Petit value of the heat capacity. Since most solids attain this condition before melting, this assumption should be acceptable for their liquids. However, this will exclude hydrogen and helium from consideration and make doubtful a few other cases including neon. Second, it will be assumed that the molecules are spherically symmetrical, either actually or by virtue of rapid and free rotation. Third, the nature of any intramolecular vibrations will be assumed to be the same whether the molecules are in the liquid or gas states. Fourth, the potential energy of an assemblage of molecules will be taken as a function only of the various intermolecular distances. As Mayer[5] has pointed out, this last consideration excludes any substances tending to form a limited number of valence bonds, but is consistent with the properties of saturated molecules where the only attractive forces are of the van der Waals-London type. Fifth, it is postulated that the potential energy for a pair of molecules can be written: $E=A\varphi(R/R_0)$ where φ is a universal function, R is the intermolecular distance, and A and R_0 are constants to be specified for each substance. Probably no group of molecules fulfills this last assumption precisely but at least the heavier rare gases satisfy it to a high degree of accuracy. Fig. 1 shows qualitatively the form of the function φ. The inverse sixth power attraction is characteristic of most, if not all, molecules forming normal liquids. Furthermore, provided that the repulsive branch is very steep, minor variations in slope should not affect the results greatly. Nothing need be said concerning the exact nature of the function φ; the only assumption is its universality. In their discussion of corresponding states for gas imperfection de Boer and Michels[1] were led to conditions essentially the same as these.

While a mathematical derivation will be given presently it seems worth while to present the following simple argument first. If two systems fulfilling the above conditions and containing equal numbers of molecules are enclosed in containers with linear dimensions proportional to the R_0's (thus volumes proportional to R_0^3), it is apparent that spacial correspondence has been attained. Since energies of motion and temperature are proportional, the corresponding temperatures will be proportional to the A's. Thus if the systems are compared at volumes bearing the same ratio to the values of R_0^3 and at temperatures thus related to the A's, then these systems should present corresponding behavior.

In more mathematical terms one may set up a classical partition function or phase integral.

$$Q=\int_0^\infty\cdots\int_0^\infty\int_0^{X_0}\cdots\int_0^{Z_0} e^{-(K.E.+P.E.)/kT} \times dp_{x_1}\cdots dp_{z_n}dx_1\cdots dz_n.$$

This partition function differs from those commonly set up for gases in that the integration is to be over the coordinates and momenta for all molecules instead of only one. The complex potential energy makes it impossible to factor out a contribution from each molecule. The kinetic energy can of course be written

$$\text{K.E.}=\frac{1}{2m}\sum_{i=1}^{n}(p_{x_i}^2+p_{y_i}^2+p_{z_i}^2).$$

The integration over momenta is then easily carried out giving:

$$Q=(2\pi mkT)^{3n/2}\int_0^{X_0}\cdots\int_0^{Z_0} e^{-P.E./kT}dx_1\cdots dz_n.$$

The potential energy is given by

$$\text{P.E.}=\tfrac{1}{2}A\sum_{i=1}^{n}\sum_{j=1}^{n}{}'\,\varphi(\Delta R_{ij}/R_0),$$

in which $\Delta R_{ij}=[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^{\frac{1}{2}}$ is the distance between molecules i and j, the

prime indicates omission of terms with i and j equal, and the factor $\frac{1}{2}$ arises because each term is taken twice. The integral for Q is thus extremely complex and no attempt will be made to evaluate it. We may rewrite it as follows however:

$$Q=\left[2\pi mkA\left(\frac{T}{A}\right)\right]^{3n/2} R_0^{3n}\int_0^{(X_0/R_0)}\cdots\int_0^{(Z_0/R_0)} \times e^{-(A/T)(1/2k)\Sigma\Sigma\varphi(\Delta R_{ij}/R_0)}d\left(\frac{x_i}{R_0}\right)\cdots d\left(\frac{z_n}{R_0}\right).$$

The integral now depends only on the value of the ratio (A/T) and upon the upper limits of integration, the latter amounting to the ratio of the volume $(V=X_0Y_0Z_0)$ to R_0^3 since the shape of the container should not be a factor. We may then write:

$$Q=(2\pi mkAR_0^2)^{3n/2}F(V/R_0^3, A/T),$$

where the (T/A) factor before the integral is now included in F. Since the thermodynamic properties of interest (excepting the absolute, third law entropy) are determined by this partition function and its temperature and volume derivatives, and since constant factors such as those before F are of no consequence, it is thus established that the behavior of all substances conforming to the above assumptions will be the same, provided they are compared at equal values of (T/A) and (V/R_0^3).

Nothing has been said concerning the exact definition of R_0 and A. Since the critical point is certainly a corresponding point, it seems logical to take the critical temperature, T_c, for A and the critical volume, V_c, for R_0^3. Then the reduced temperatures and volumes will be those in common usage. Recent experiments of Maass and co-workers[8] and theoretical considerations of Mayer and Harrison[5] show that the behavior of substances near the critical point is more complex than had been assumed earlier. Nevertheless, this seems the best point to take as a standard. As will be shown later, the behavior of actual liquids can be compared conveniently without reference to critical point data.

The present and principal interest in the above considerations is with respect to the liquid state, and the term "perfect liquid" is proposed for substances following this behavior. Although the vapor of a perfect liquid is not necessarily a perfect gas, nevertheless this usage of terms will be very similar. Thus the term perfect gas, suggests a behavior representable by an equation which all gases follow more or less closely. Similarly the term perfect liquid, refers to a behavior which all normal liquids follow more or less closely.

The heavier rare gases are the substances which may be expected to show most perfect behavior in the above sense, and their properties will now be considered in order both to verify the theory and to prepare tables describing perfect behavior.

First considering vapor pressure, precise data covering the entire liquid range are available for argon and krypton, the latter from recent measurements by Meihuizen and Crommelin.[9] For argon, and in fact wherever other references are not given, the data have been taken from the *International Critical Tables*, or in a few cases from the Landolt Börnstein *Tabellen*. Fig. 2 shows these vapor pressure data, together with less precise data for xenon. Also included are the values for neon which show a deviation attributable to the failure of classical mechanics, and the values for methane which show good agreement due possibly to a cancellation of small errors arising from quantum effects and restriction of rotation. The agreement between the

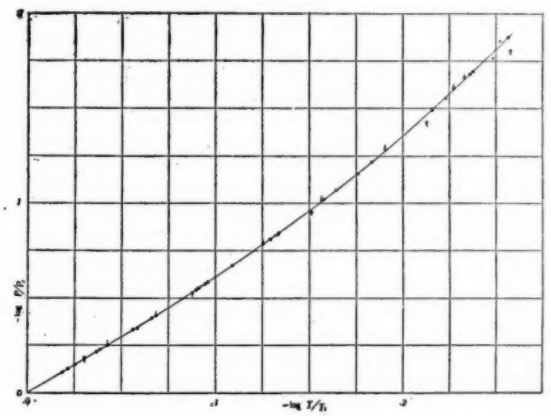

FIG. 2. Reduced vapor pressure data: 0 argon, ● krypton, x xenon, ♀ neon, ♁ methane.

[8] Maass and Geddes, Phil. Trans. Roy. Soc. London **A236**, 303 (1937) and earlier work there listed.

[9] Meihuizen and Crommelin, Physica **4**, 1 (1937)

precise data for argon and krypton is remarkable, the largest deviations being considerably less than 0.1 percent if attributed to the temperature. The equation given for krypton by Meihuizen and Crommelin[9] was put into the reduced form and taken as representative.

$$\log_{10}\pi = \frac{4.29810}{\theta} - 12.55400\log\theta + 0.63158 + 3.66652\theta,$$

where $\pi = p/p_c$ and $\theta = T/T_c$.

While the exact correspondence of the vapor pressure curves requires that the entropies of vaporization also correspond, it is worth while to present independent calorimetric values. The data in Table I are in part from calorimetric heats of vaporization and in part calculated from statistical entropies of the vapor and third law entropies of the liquid. In both cases they are for vaporization to the real gas. For comparison, values are given at the boiling points (Trouton's Rule) and at constant vapor density (Hildebrand's rule). The basis of comparison selected for the present theory is $\theta(=T/T_c)$ equal to 0.56 or the equivalent, a gas to liquid volume ratio of 335. The marked disagreement in the case of neon is to be ascribed to a failure of classical mechanics. The heat capacities of the liquids are also included, the value for neon being again low. The heat capacity of argon also appears to be slightly low.

Figure 3 shows the gas and liquid densities as a function of reduced temperature and Fig. 4 shows the gas to liquid volume ratio. These data are less precise than those on vapor pressure. However, the agreement appears to be rather satisfactory.

TABLE I. *Entropies of vaporization of perfect liquids.**

SUBSTANCE	ΔS_{VAP} $V_{GAS}/V_{LIQ}=335$	B. P.	$V_{GAS}=10$ l.	$C_{p\,LIQ}$
Neon	(17.95)	15.0	(19.3)	8.9
Argon	18.67	18.0	19.0	10.1
Krypton	18.60	18.1	18.5	10.6
Xenon	18.66	18.4	18.0	10.7

* (Ne, A, Kr) K. Clusius, Zeits. f. physik. Chemie **B31**, 459 (1936); (Kr) Clusius, Krius and Konnertz, Ann d. Physik (S)**33**, 642 (1938); (Xe) K. Clusius and Riccoboni, Zeits. f. physik. Chemie **B38**, 81 (1937). The values for Ne at 10 l. gas volume and at $V_{gas}/V_{liq}=335$ are extrapolated.

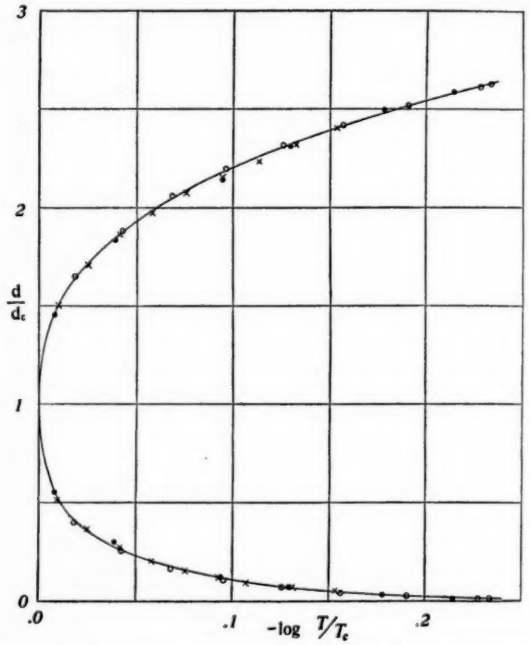

FIG. 3. Reduced density data: ● argon, 0 methane, x xenon.

These various data are combined to give the behavior of the perfect liquid. The vapor pressure equation has been given already. Other data are included in Table II. The accuracy of the various values is roughly indicated by the number of significant figures given, the error being usually confined to the last figure. It should be remembered that the true entropies of vaporization are given; these values are from three to ten percent lower than would be obtained from vapor pressures if the perfect gas law were assumed and the liquid volume neglected.

While Table II is presented in terms of reduced temperature, θ, certain of the other quantities are equally satisfactory for specifying corresponding states. In particular the gas to liquid volume ratio (last column) varies rapidly with temperature and involves no measurements at the critical point. Thus it is to be especially recommended for the comparison of various substances, inasmuch as the critical point data are likely to be unavailable or inaccurate in some cases.

So long as classical mechanics still holds, the behavior of substances fulfilling our conditions should also correspond in the solid state. Actually quantum-mechanical effects enter so soon that

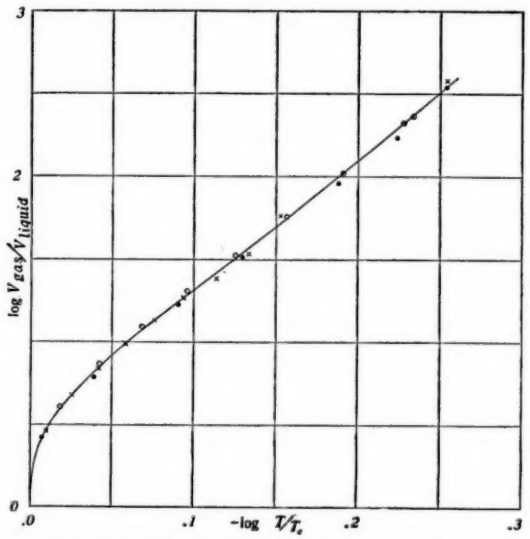

FIG. 4. Gas to liquid volume ratio as a function of reduced temperature: ● argon, 0 methane, x xenon.

this idea will have little practical interest. However, a few valid conclusions can be drawn. First, all perfect liquids will freeze into cubic closest packed (face-centered) crystals. Also, the entropy of fusion, and the triple point temperatures show regularities as exhibited in Table III.

In closing, Part I may be summarized by saying that when certain conditions are met, statistical mechanics requires a rather complete correspondence in the behavior of the liquid and gaseous substances. While it is realized that the available group of substances may not exactly fulfill the required conditions, nevertheless the observed correspondence is sufficiently exact that this idea of a perfect liquid behavior will probably be useful for some time.

PART II

Imperfect liquids

In Part I it was shown that there would be a rather complete correspondence in the behavior of liquids fulfilling certain assumptions, and the name perfect liquids was suggested for these. The deviation in behavior will now be considered for substances which fail to satisfy these conditions completely. These deviations can be best classified in terms of the requirement violated. The five requirements of perfection may be briefly restated as follows: (1) The validity of classical statistical mechanics, (2) spherical or freely rotating molecules, (3) intramolecular vibration same in liquid and gas, (4) potential energy depending only on intermolecular distances, and (5) universal shape of potential curve.

Since we were unable to calculate the perfect behavior theoretically we shall not expect to derive exact expressions for the deviation in the various cases. The discussion of these deviations is further complicated by the fact that whenever a source of imperfection exists, it usually causes all the properties of the liquid to deviate, so that none are left to specify the proper conditions for comparison. The best that can be done is to select some properties that are relatively sensitive to imperfection and insensitive to temperature, and compare these properties at points chosen by the use of properties of the opposite character. Also, it is possible to be consistent, which will assure that the more imperfect substances will deviate more.

Since the entropy of a gas depends particularly on its volume, and because imperfection cannot change the liquid volume very greatly, it seems best to compare entropies of vaporization at an equal vapor to liquid volume ratio. This basis is, moreover, a very convenient one. The change in heat capacity with vaporization is relatively insensitive to the temperature, and will be taken at the same point. Unless it is stated otherwise, the volume ratio 335 will be used.

These two properties (heat capacity and entropy of vaporization) will receive most attention in the following discussions. Since either may be

TABLE II. *The behavior of the perfect liquid.*

$\theta = T/T_c$	$-\log \theta$	$-\log \pi$ $(\pi = p/p_c)$	ΔS_{VAP}	$C_{s(TR)}$	ϕ LIQ $(\phi = V/V_c)$	$\frac{V_{GAS}}{V_{LIQ}} = \frac{d_{LIQ}}{d_{GAS}}$
0.56	0.25181	1.8291	18.68	10.7	0.376	335
.57	0.24413	1.7542	18.20	10.7	0.379	290
.58	0.23657	1.6825	17.72	10.7	0.382	250
.59	0.22915	1.6134	17.25	10.7	0.385	215
.60	0.22185	1.5469	16.82	10.7	0.387	187
.62	0.20761	1.4213	15.95		0.392	142
.64	0.19382	1.3044	15.18		0.398	110
.66	0.18046	1.1953	14.42		0.404	84
.68	0.16749	1.0933	13.73		0.410	67
.70	0.15490	0.9974	13.11		0.417	53
.75	0.12494	0.7808			0.437	31
.80	0.09691	0.5912			0.461	19
.85	0.07058	0.4224			0.490	12
.90	0.04576	0.2697			0.531	7.3
.95	0.02228	0.1298			0.596	4.2
1.00	0.00000	0.0000			1.000	1.0

$p_c V_c / T_c = 23.9$ cc atmos. per degree Kelvin.

TABLE III. *Data on the freezing of perfect liquids.**

SUBSTANCE	ΔS_{FUSION} CAL./DEG.	$\theta = T/T_c$ T.P.
Argon	3.35	0.557
Krypton	3.37	0.554
Xenon	3.40	0.557

* See footnote to Table I.

taken as a measure of imperfection, a check of one against the other will offer a check on the explanations offered. In Fig. 5 deviations in entropy are plotted against deviations in heat capacity for several substances of various types. An abnormally large entropy of vaporization, and an abnormally large liquid heat capacity are indicated as positive deviations, respectively.

Quantum-mechanical effects

The failure of neon to follow perfect behavior exactly has already been ascribed to quantum-mechanical effects. The deviation of hydrogen and helium are of course even more marked. As pointed out by Byk,[10] the following parameter can be said to measure the extent of quantum deviations: $(mkT)^{\frac{1}{2}}V^{\frac{1}{3}}/h$. An equivalent quantity which is convenient for our purposes is $M^{\frac{1}{2}}T_c^{\frac{1}{2}}V_c^{\frac{1}{3}}$. Table IV gives values of this parameter for a representative group of substances.

Some of the substances in Table IV are, of course, imperfect for other reasons than quantum-mechanical deviations. They are included now so that an estimate may be made of the quantum-mechanical contribution to their total imperfection.

While, as stated above, we shall not expect to predict the exact deviations caused by quantum effects, some approximate arguments can be given. In many respects the nature of a liquid and solid are similar. It has been commonly assumed in treating liquids that most of the time a molecule vibrates within a cage of neighboring molecules in about the same manner as in the solid. Thus if the ability of molecules in the liquid to occasionally jump from cage to cage is of no particular significance to the property of interest, the difference between liquid and solid may be slight. With this idea in mind, we shall take the well-known Debye functions for a somewhat idealized solid, and apply them to the liquid. The last two columns of Table IV were obtained in this manner, by taking the -1.8 cal. per degree deviation in the heat capacity of neon as a standard. The changes in C_p and S are in opposite directions. The heat capacity becomes too small and the entropy of the liquid becomes too large. This leaves the entropy of vaporization too small.

The liquid volume is also affected similarly. Quantum-mechanical effects cause the volume to remain too large and the coefficient of expansion to become too small. This, of course, changes the gas to liquid volume ratio which was taken as a standard for comparing entropies. The liquid volume of neon is about three percent too large at its triple point, and this change affects the entropy by less than 0.1 cal. per degree, which is almost negligible. The experimental entropy of vaporization of neon deviates from the perfect by 0.7 cal. per degree as compared to the calculated 1.0, which is probably as good agreement as can be expected.

Hydrogen and helium are so much affected by quantum considerations that it is not worth while to discuss them in detail here.

TABLE IV. *Quantum-mechanical effects.*

SUBSTANCE	$(M^{\frac{1}{2}}T_c^{\frac{1}{2}}V_c^{\frac{1}{3}})$	$-\delta C_{DEBYE}$	δS_{DEBYE}
Helium	17.6		
Hydrogen	32.6		
Neon	104	(1.8)	1.0
Methane	256	0.4	0.2
Nitrogen	266	0.3	0.2
Oxygen	295	0.3	0.1
Argon	328	0.2	0.1
Ethane	491	0.1	0.1
Lithium	500	0.1	0.1
Krypton	600	0.1	0.0
Xenon	940	0.0	0.0
Mercury	2000	0.0	0.0

Restriction of rotation

Turning now to substances whose principal imperfection arises from a restriction of rotation of the molecules in the liquid, we shall again present only a rough theoretical consideration. Thermodynamic functions for restricted rotational degrees of freedom are available[11] for the case of one-dimensional rotation. The results for

[10] Byk, Ann. d. Physik **66**, 167 (1921); **69**, 161 (1922).

[11] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).

the two- and three-dimensional cases are probably similar within the degree of accuracy that a simple assumed potential function fits the case at hand. The curves rising to the right in Fig. 5 were drawn by taking two or three times the deviation for a single degree of freedom, respectively.

The points on Fig. 5 for such substances as the hydrogen halides, nitrogen, carbon monoxide, carbon disulfide, chlorine and bromine fit the curve for two degrees of restricted rotation reasonably well. Similarly, phosphine, hydrogen sulfide, ethane ethylene and tetramethyl methane fit the curve for three degrees of restricted rotation satisfactorily.

It is noteworthy that the substances in which restriction arises from dipolar effects fall in Fig. 5 along with those in which restriction arises from nonspherical shape.

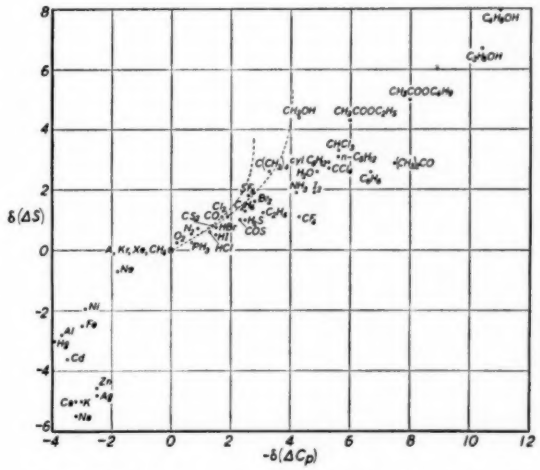

FIG. 5. The behavior of imperfect liquids. The deviations from the perfect entropy of vaporization are plotted against the derivations from perfect change of heat capacity with vaporization. The dotted lines show the expected position of points if the only imperfection is restricted rotation of molecules in the liquid. The left curve is for two-dimensional rotation, the right curve, for three. The points for all perfect substances lie at the origin.

Change of intramolecular vibrations

It is apparent that many of the points on the right side of Fig. 5 fall below and to the right of the curves for restricted rotation. This is explicable in a general way when the numerous intramolecular motions of complex molecules are considered. While intermolecular forces have little effect on the principal valence bond vibrations, these forces may seriously change the torsional motion about bonds and the bending of long chains. On the whole, the frequencies of these vibrations should be lowered in the liquid, and this will lead to a higher liquid heat capacity (larger $-(\Delta C_p)$) and a larger liquid entropy (smaller (ΔS)).

This effect is particularly marked for long chain molecules, also in *n*-pentane as compared to neo-pentane (tetramethyl methane).

At this point a few remarks seem in order concerning the very normal position taken by water in Fig. 5. The gas to liquid volume ratio becomes 335 at slightly above 150°C and at this temperature most of the molecules are probably rotating. The observed normal behavior is then to be expected. It seems that the small molal volume of water as compared to that of most substances boiling near 100°C (18 cc compared to about 100 cc) led to the view that water was very abnormal.

The position O_2 in Fig. 5 suggests almost perfect behavior for this paramagnetic molecule. This view would be confirmed by the volume and coefficient of expansion behavior. However, the melting point of O_2 is much too low. In this respect it deviates from perfect behavior much more than N_2, CO, HI, and other similar substances. Thus the apparent perfection of O_2 is probably to be regarded as an accidental cancellation of deviations in different directions.

Metals

While it may be doubtful which assumptions the metals violate, in any case they form a group and should be considered together. Experimentally, their entropies of vaporization are much less than perfect and vary over a considerable range. The decrease of heat capacity with vaporization is also less than perfect, but is about the same for most metals. Another notable "imperfection" of the metals is their relatively low melting points. Many melt at temperatures less than half that corresponding to the perfect behavior. The coefficient of expansion is considerably smaller for metals than for chemically saturated substances.

Table IV shows that even lithium is essentially unaffected by quantum considerations, and it seems unlikely that lack of spherical symmetry

can be an important consideration in many cases. On the other hand, the possibility of thermal excitation of electronic motion may be important. Also, metallic binding forces are quite different from the London-van der Waals forces of the saturated molecules. The assumption that the potential energy can be expressed in terms of intermolecular distances alone is no longer valid.

A recent paper by Pauling[12] presents a most interesting and enlightening view with respect to metallic binding. He considers electron pair bonds of the ordinary type to be resonating among a large number of possible positions. Thus, when a given atom has as many neighbors as it has electrons to share, the full number of bonds can form. Further, neighbors lead to decrease in energy due to resonance, but this effect will probably soon show a saturation. In other words, a given atom has a greater affinity for its first few neighbors than for the eleventh or twelfth. Since arrangements with somewhat less than twelve coordination probably afford more freedom of motion and consequently greater entropy,[13] they will be assumed at the higher temperatures. Also, because of this saturation of binding energy, they will be assumed sooner in the case of the metal than in the perfect substance. Thus the low melting points of metals and the larger liquid entropies (lower ΔS vap.) are to be expected.

The relative entropies within the metals are in general accord with this idea. Thus iron and nickel, to which Pauling attributes about six bonding electrons, are more nearly perfect than the alkali metals with but one. On the other hand, zinc, cadmium and mercury with similar electronic structures show considerable variation.

The entropy attributable to electronic motion through the metal will be removed by vaporization, and should therefore reduce the total entropy of vaporization. The magnitude of this effect should be about one cal. per degree or less[14] and is alone insufficient to explain the observed results. It undoubtedly contributes, however.

While it seems likely that a single function φ will be quite general for van der Waals forces, there is no reason to believe that this same function will be satisfactory for metallic binding. In particular, if the function for metals were more symmetrical near the minimum, the smaller coefficient of expansion and smaller liquid heat capacity would be explained.

On the whole it seems as if the nature of liquid metals will have to be treated as an almost independent problem.

Before concluding, it seems desirable to discuss briefly the Hildebrand rule[2] for entropies of vaporization. The great success of this rule together with the encouragement of its author led to this investigation. In the light of the above results, the selection of a constant molal gas volume rather than a constant pressure is completely justified. On the other hand, it appears that one should actually take a constant gas to liquid volume ratio as the criterion. Many simple liquids boiling somewhat above room temperature, have about the same molal volumes, and in such cases the Hildebrand rule will be essentially the same as the one here proposed. It was such a group of substances that Professor Hildebrand recently discussed.[7]

In conclusion, it is hoped that the ideas of Part I will serve as a foundation for relatively precise discussions of the behavior of actual liquids. The second part of this paper has merely outlined some more obvious principles. Further experimental investigations of the properties of the perfect substances would also seem to be very worth while.

[12] L. Pauling, Phys. Rev. **54**, 899 (1938).
[13] O. K. Rice, J. Chem. Phys. **7**, 136 (1939).
[14] W. M. Latimer, J. Am. Chem. Soc. **44**, 2136 (1922).

Thermodynamics of Crystals and Melting

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The Helmholtz free energy, A, of a rigid body is a function of temperature, and of the six homogeneous strain components. If the crystal is to be rigid, three inequalities must be satisfied for the derivatives of A with respect to the six strain components, for a regular (cubic) lattice. This enables one to limit the pressure-temperature range for which the crystal is stable. The violation of the condition $c_{44}>0$, that the crystal resist shearing, is interpreted as leading to melting. From a knowledge of the forces between the molecules the phase integral, and therefore the free energy, may be calculated as a function of T, V, and the six strain components. The numerical calculations are carried out for a body-centered cubic lattice. The product of all the frequencies is calculated directly, so that the assumption that the Debye equation for the frequency distribution holds, is not necessary. The melting curve, pressure against temperature, is then determined.

THERE exist many attempts to derive theoretically the laws of melting. I mention Lindemann's[1] formula, Grüneisen's[2] general thermodynamics of isotropic solids, the theories of Braunbeck,[3] Raschevsky[4] and of Herzfeld and Goeppert-Mayer.[5] The newest contribution to this problem is an ingenious paper of Lennard-Jones and Devonshire[6] who apply the "method of order and disorder" invented by Bragg and Williams.[7]

All these papers use different "criteria" of melting: e.g. Lindemann, the collision of a vibrating molecule with its neighbor; Raschevsky, the instability of a particle under the action of its neighbors; Braunbeck, the instability of the vibration of two rigid simple lattices against one another; Herzfeld and Goeppert-Mayer, the minimum of pressure with respect to changes of volume; Lennard-Jones, the transition of the structure from order into disorder.

In actual fact there can be no ambiguity in the definition of, or the criterion for, melting. The difference between a solid and a liquid is that the solid has elastic resistance against shearing stress while the liquid has not. Therefore, *a theory of melting should consist of an investigation of the stability of a lattice under shearing stress*. As far as I know, the only author who has made an attempt to apply this natural definition of melting is Brillouin.[8] The short published account of his considerations indicates that he uses Debye's approximation for calculating the frequencies of the crystal; this method is objectionable, not only because it neglects the short waves, but because it does not lead to a reduction of the observable quantities to atomic forces.

Independently of this work of Brillouin, I have developed a method for treating thermodynamics of a crystal lattice in such a way that the formulae are valid over a wide range of temperature, in the hope that this range might include the melting point.

This theory is in some way the counterpart of Mayer's rigorous treatment[9] of condensing gases where the liquid state was reached from the other side, at least in so far as the existence of a condensation point could be proved with the methods of kinetic theory of gases.

The chief point in our method is the clear distinction between *molecular variables* and *molar parameters* as defined in statistical mechanics. The molecular variables are the generalized coordinates and conjugate momenta q_1, p_1; q_2, p_2; $\cdots$ which are distributed at random according to statistical laws. The molar parameters $a_1, a_2, \cdots$ describe the (macroscopic) external influences on the system (e.g. the volume of a gas). The energy of the system depends on both

[1] F. A. Lindemann, Physik. Zeits. **11**, 609 (1910).
[2] E. Grüneisen, Ann. d. Physik (4) **39**, 257 (1912).
[3] W. Braunbeck, Zeits. f. Physik **38**, 549 (1926).
[4] N. v. Raschevsky, Zeits. f. Physik **40**, 214 (1927).
[5] K. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934).
[6] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A169**, 317 (1939).
[7] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934); **151**, 540 (1935); **152**, 230 (1935).
[8] L. Brillouin, Phys. Rev. **54**, 916 (1938).
[9] J. Mayer, in collaboration with Ph. G. Ackermann and S. F. Harrison, J. Chem. Phys. I, **5**, 67; II, **5**, 74 (1937); III, **6**, 87; IV, **6**, 101 (1938).
See also M. Born and K. Fuchs, Proc. Roy. Soc. **A166**, 391 (1938); B. Kahn and G. E. Uhlenbeck, Physica V **4**, 399 (1938).

kinds of variables, $\epsilon(q_1, p_1; q_2, p_2; \cdots; a_1, a_2, \cdots)$. If it is given, we can construct the partition function which for high temperatures is given by the law of classical statistical mechanics:

$$Q(a_1, a_2, \cdots; T) = \int\cdots\int dq_1 dp_1 dq_2 \cdots \times e^{-\epsilon(q_1, p_1; q_2\cdots; a_1\cdots)/kT}. \quad (1)$$

Then the free energy of the system is

$$A = -kT \log Q, \quad (2)$$

and all other thermodynamic properties are found by differentiation:

$$\begin{aligned} &\text{the entropy} \quad S = -\partial A/\partial T, \\ &\text{the energy} \quad E = A + TS, \end{aligned} \quad (3)$$

the generalized forces corresponding to the molar parameters:

$$F_r = -\partial A/\partial a_r. \quad (4)$$

If we want to apply this prescription to a crystal lattice we must clearly state which are the molar parameters. For the sake of simplicity let us consider only a cubic lattice of the Bravais type (simple, face-centered or body-centered). As thermodynamics has only to do with states of equilibrium (from the macroscopic, or molar, standpoint) we can restrict our considerations to homogeneous deformations. Then the cubic cell (with the side a) becomes a general parallelepiped, described by three vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ with six essential parameters (invariant with respect to rigid motions), *viz.* three lengths and three angles, or the six scalar products of the vectors with one another

$$\mathbf{a}_1^2, \mathbf{a}_2^2, \mathbf{a}_3^2, \quad \mathbf{a}_2\cdot\mathbf{a}_3, \quad \mathbf{a}_3\cdot\mathbf{a}_1, \quad \mathbf{a}_1\cdot\mathbf{a}_2.$$

The shape of the cell, i.e., these six parameters, are given by macroscopic (homogeneous) deformation and play the part of molar parameters. The actual positions of the particles can be described by displacement vectors relative to the deformed cell, $\mathbf{u}^l$, where the index l stands for three integers l_1, l_2, l_3 defining a lattice point. The energy is a function of all the $\mathbf{u}^l$ and the $\mathbf{a}_1^2, \cdots \mathbf{a}_2\cdot\mathbf{a}_3, \cdots$. If we develop it with respect to powers of the $\mathbf{u}^l$ the linear terms vanish in consequence of the symmetry of the lattice, and the quadratic terms allow the introduction of normal coordinates which can be used, instead of the $\mathbf{u}^l$, also in the higher terms. Then the integration in (1) can be performed, at least in principle, and leads to

$$A = A(T, \mathbf{a}_1^2, \mathbf{a}_2^2, \mathbf{a}_3^2, \mathbf{a}_2\cdot\mathbf{a}_3, \mathbf{a}_3\cdot\mathbf{a}_1, \mathbf{a}_1\cdot\mathbf{a}_2). \quad (5)$$

It is evident that A is proportional to the number N of the particles (if surface effects are neglected). We introduce, instead of the $\mathbf{a}_1^2$, $\cdots$ $\mathbf{a}_2\cdot\mathbf{a}_3$, $\cdots$ the side of the cube of the original (undeformed) cell and the six dimensionless *strain components**

$$\begin{aligned} 2x_x &= e_{11} = (\mathbf{a}_1^2 - a^2)/a^2, & y_z &= e_{23} = \mathbf{a}_2\cdot\mathbf{a}_3/a^2, \\ 2y_y &= e_{22} = (\mathbf{a}_2^2 - a^2)/a^2, & z_x &= e_{31} = \mathbf{a}_3\cdot\mathbf{a}_1/a^2, \\ 2z_z &= e_{33} = (\mathbf{a}_3^2 - a^2)/a^2, & x_y &= e_{12} = \mathbf{a}_1\cdot\mathbf{a}_2/a^2, \end{aligned} \quad (6)$$

and write

$$A = Nf(T, a, x_x, y_y, z_z, y_z, z_x, x_y). \quad (7)$$

The function f depends on T and 7 geometrical variables, but only six of the latter are essential; there exists a linear identity between the seven first derivatives of f,

$$a\partial f/\partial a = (2x_x+1)\partial f/\partial x_x + \cdots + 2y_z\partial f/\partial y_z + \cdots.$$

By repeated differentiation one gets identities between the higher derivatives. We write down the two equations which hold for the first and second derivatives in the case $x_x = 0$, $\cdots$ $y_z = 0$, $\cdots$,

$$\begin{aligned} a\frac{\partial f}{\partial a} &= \frac{\partial f}{\partial x_x} + \frac{\partial f}{\partial y_y} + \frac{\partial f}{\partial z_z}, \\ a^2\frac{\partial^2 f}{\partial a^2} - a\frac{\partial f}{\partial a} &= \frac{\partial^2 f}{\partial x_x^2} + \frac{\partial^2 f}{\partial y_y^2} + \frac{\partial^2 f}{\partial z_z^2} \\ &\quad + 2\frac{\partial^2 f}{\partial y_y \partial z_z} + 2\frac{\partial^2 f}{\partial z_z \partial x_x} + 2\frac{\partial^2 f}{\partial x_x \partial y_y}. \end{aligned} \quad (8)$$

If we develop f for a given value of a into a power series of the $x_x, \cdots y_z, \cdots$ the result must have, for a cubic lattice, the form

$$\begin{aligned} f = f_0 &+ f_1\cdot(x_x + y_y + z_z) \\ &+ \tfrac{1}{2}\{f_{11}\cdot(x_x^2 + y_y^2 + z_z^2) \\ &+ 2f_{12}\cdot(y_y z_z + z_z x_x + x_x y_y) \\ &+ f_{44}\cdot(y_z^2 + z_x^2 + x_y^2)\} + \cdots, \end{aligned} \quad (9)$$

* We use two different notations, that of Voigt: $x_x, \cdots, y_z, \cdots$, and that of Brillouin: $e_{11}, \cdots, e_{23}, \cdots$. It is essential to define the strain components for finite deformations, as we have done here, not in the usual way for small displacements.

where $f_0, f_1, f_{11}, f_{12}, f_{44}$ are functions of a and T; the relations (8) become

$$a\partial f_0/\partial a = 3f_1, \quad a^2\partial^2 f_0/\partial a^2 = 3\{f_1+f_{11}+2f_{12}\}; \quad (10)$$

the latter can also be written

$$a\partial f_1/\partial a = 2f_1+f_{11}+2f_{12}. \quad (10a)$$

The density of free energy is A/V where V is the volume containing N particles. Let γ be the number of cells a^3 corresponding to one particle, then $V=\gamma Na^3$. The value of γ differs for the different cubic lattices; if a is always the projection of the smallest distance on the side of the cube, we have for the simple cubic lattice: $\gamma=1$; body-centered: $\gamma=4$; face-centered: $\gamma=2$. Now we get for the *density of free energy*

$$\frac{A}{V}=\frac{f}{\gamma a^3}=\frac{f_0}{\gamma a^3}-p\cdot(x_x+y_y+z_z) + \tfrac{1}{2}\{c_{11}(x_x^2+y_y^2+z_z^2) + 2c_{12}(y_yz_z+z_zx_x+x_xy_y) + c_{44}(y_z^2+z_x^2+x_y^2)\}+\cdots, \quad (11)$$

where

$$-p=(1/\gamma a^3)f_1(a, T), \quad (12)$$

$$c_{11}=(1/\gamma a^3)f_{11}(a, T),$$
$$c_{12}=(1/\gamma a^3)f_{12}(a, T), \quad (13)$$
$$c_{44}=(1/\gamma a^3)f_{44}(a, T).$$

The derivatives of A/V with respect to $x_x, \cdots y_z, \cdots$ are the negative components of the stress tensor:

$$-X_x=-p+c_{11}x_x+c_{12}(y_y+z_z)+\cdots, \quad \vdots \quad -Y_z=c_{44}y_z+\cdots. \quad (14)$$

We see that the stress does not vanish for $x_x=0, \cdots y_z=0, \cdots$ but goes over into a uniform pressure $p=X_x=Y_y=Z_z$. This must be so as the constant a of the cubic lattice, to which the stress $X_x, \cdots Y_z, \cdots$ is applied, is not assumed to be that of equilibrium under zero pressure. Our theory corresponds exactly to the experimental conditions under which Bridgman and others[10] have recently worked, namely a combination of hydrostatic pressure and other stresses.

The formula (12) is evidently the *equation of state* for the cubic crystal giving a as a function of p, T, hence the thermic expansion for any pressure.

c_{11}, c_{12}, c_{44} are the elasticity constants in Voigt's notation for a given temperature and external hydrostatic pressure.

The stability conditions, which guarantee that the quadratic terms in (11) are positive definite,* are

$$\frac{3}{\kappa}=c_{11}+2c_{12}>0, \quad c_{11}-c_{12}>0, \quad c_{44}>0, \quad (15)$$

where κ is the cubic compressibility. The identities (10), (10a) allow us to write the equation of state and the expression for the compressibility in the form

$$p=\frac{1}{3\gamma a^2}\frac{\partial f_0}{\partial a}, \quad \frac{3}{\kappa}=\frac{1}{\gamma a^3}\left(a\frac{\partial f_1}{\partial a}-2f_1\right)=\frac{\partial(ap)}{\partial a}, \quad (16)$$

which can be used for checking calculations.

We now discuss the different possibilities for instability of the lattice if temperature increases.

I. The normal case will be that where the stability against shearing stress vanishes first, $c_{44}=0$. According to our previous considerations this means *melting*.

The *melting curve* is given by the two equations

$$f_1(a, T)=-a^3\gamma p, \qquad f_{44}(a, T)=0. \quad (17)$$

The second one gives $a(T)$, and if we introduce this in the first equation we get $p(T)$.

II. It might happen that $c_{11}=c_{12}$ is satisfied first so that the two equations

$$f_1(a, T)=-a^3\gamma p, \quad f_{11}(a, T)-f_{12}(a, T)=0 \quad (18)$$

are satisfied. This means the transition of the solid into a state in which the stress is a hydro-

[10] P. W. Bridgman, Am. J. Sc. **36**, 81 (1938). J. App. Phys. **9**, 517 (1938). Mech. Eng. p. 107 (1939). Here a list of the literature is published.

* Our minimum problem is not quite of the usual type because the variables a, x_x, $\cdots$, y_z, $\cdots$ are not independent; $x_x+y_y+z_z$ is the relative change of volume which can also be expressed as $3\delta a/a$. The orthodox way of treating the problem is this: We consider only 6 variables, say a, x_x, y_y, y_z, z_x, x_y by eliminating z_z with the help of $x_x+y_y+z_z=0$. Then x_x, y_y are independent just as y_z, z_x, x_y. The linear terms in (11) vanish, and the quadratic terms can be written in the form

$$\tfrac{1}{4}(c_{11}-c_{12})\cdot\{3(x_x+y_y)^2+(x_x-y_y)^2\}+\tfrac{1}{2}c_{44}(y_z^2+z_x^2+x_y^2);$$

this gives the second and third of the conditions (15). The first follows directly by developing with respect to a and using (16).

static pressure (as in a liquid) but nevertheless an elastic resistance against shearing survives. I suggest calling this state a "*gel*."

Dr. K. Fuchs has directed my attention to the fact that there are indications of the existence of such a state even for metals. Measurements of the elastic constants of the *alkali metals* Na and K made by Bender[11] have shown that the difference $c_{11}-c_{12}$ is unusually small. Bidwell[12] has measured electric resistance and thermoelectric power of these metals at various temperatures and found a change of slope at about 100° below the melting point indicating a transformation; but a study of the structure with the help of x-rays showed no change of the lattice type, but only an "obliteration" of the structure.

III. If $c_{11}+2c_{12}=0$ is satisfied first so that

$$f_1(a, T)=-a^3\gamma p,\quad f_{11}(a, T)+2f_{12}(a, T)=0, \tag{19}$$

the lattice is completely unstable and has no cohesion at all.

This can be interpreted as *sublimation*; but a complete coincidence with the observed sublimation curve can hardly be expected because the representation of the phase space by the normal coordinates of a lattice excludes just that part of it which is characteristic for the gaseous state, namely the domain corresponding to free particles. The curve (19) will give a finite value of T_s for $p\to 0$ (just as the melting curve (17)) whereas the real sublimation curve runs into the point $T=0$, $p=0$. Nevertheless I think that for high temperatures, near the melting curve, the formulae (19) might give a fair approximation of the sublimation curve.

If these curves intersect there exists a *triple point*, the solution of the three equations:

$$f_1(a, T)=-a^3\gamma p,\qquad f_{44}(a, T)=0,$$
$$f_{11}(a, T)+2f_{12}(a, T)=0. \tag{20}$$

But it also is possible that these equations have no solution (for positive values of a, p, T); such a crystal would never melt but only sublime (as diamond, for all attainable pressures).

Two other triple points can exist, with respect to the "gel" state.

Entropy S and *energy* E are obtained in the usual way:

$$S=-\left(\frac{\partial A_0}{\partial T}\right)_a=-N\left(\frac{\partial f_0}{\partial T}\right)_a,$$
$$E=A_0+TS=N\left\{f_0-T\left(\frac{\partial f_0}{\partial T}\right)_a\right\}. \tag{21}$$

The specific heats c_v, c_p can also be expressed by differentiating E with respect to T either with $a=$const., or with $p=$const. using the equation of state (13).

A calculation of the latent heat of melting* is not possible without a knowledge of the corresponding formulae for the liquid state which our theory does not provide.

The thermodynamical properties of the crystal isolated or in equilibrium with its liquid can be expressed in terms of the functions $f_0, f_1, f_{11}, f_{12}, f_{44}$ of a and T and their derivatives. We proceed now to derive explicit expressions for these. For this purpose we have to make *approximations of a different kind*.

The first approximation is the assumption that the *thermic motion can be considered as harmonic*. To justify this step we recall the simple model of Debye consisting of one particle moving in a nonlinear field of force. He uses this to explain the thermal expansion as the shift of the mean position due to the asymmetry of the amplitude in the nonharmonic field, and he shows that the vibration about this (shifted) mean position can be considered as harmonic. The situation becomes much clearer in the case of a real lattice if we distinguish sharply between molar pa-

[11] O. Bender, Ann. d. Physik **5**, 359 (1939), gives the following experimental data for Na and K (in units of 10^{11} dynes/cm^2), to which are added the theoretical values for Li (K. Fuchs, Proc. Roy. Soc. **A157**, 444 (1936)).

	$c_{11}-c_{12}$	c_{44}
Na	0.166	0.618
K	0.087	0.263
Li	0.341	1.329

This gives for $(c_{11}-c_{12})/c_{44}$ the values 0.27, 0.33, 0.26 in Na, K, Li, respectively. In general the value of the ratio is about ten times larger, e.g. 2.7 for rocksalt, 5.4 for sylvin, 3.5 for fluorite.

[12] C. C. Bidwell, Phys. Rev. **23**, 357 (1924); **27**, 381 (1926).

* L. Brillouin, reference 8, says that a theory which considers melting as vanishing of shearing elasticity does not lead to a latent heat. This is quite correct insofar as an approach to any equilibrium from one side is insufficient for calculating the latent heat; but such a theory is not in contradiction with the existence of a latent heat (as, for instance, is the case for some types of so-called λ-point transitions).

rameters—the dimensions of the cell (corresponding to the mean position in Debye's model) —and the vibrating coordinates proper. Even if we assume the law of force for the latter to be linear, the averaged force acting on the molar parameters becomes nonlinear, and this suffices to explain thermic expansion. We shall show, moreover, that it also suffices to give a qualitative explanation of melting. Whether these formulae are accurate enough for quantitative purposes can only be judged after a thorough investigation which we shall carry out later. In any case, there is no difficulty in principle in developing the free energy for nonharmonic vibrations.

For harmonic vibrations a well-known procedure leads to the following expression for the free energy:[13]

$$A=\Phi_0+3NkT\log\frac{\hbar\bar{\omega}}{kT}, \tag{22}$$

where Φ_0 is the potential energy of the nonvibrating, but homogeneously deformed lattice, $\bar{\omega}$ a mean frequency (per 2π seconds) given by

$$\log\bar{\omega}=\tfrac{1}{6}\langle\log|[x,y]|\rangle_{Av}-\tfrac{1}{2}\log\mu. \tag{23}$$

Here μ is the mass of the particles; the average is taken over the phases α_1, α_2, α_3 of the waves,

$$f=\frac{1}{(2\pi)^3}\int_{-\pi}^{+\pi}\!\!\int\!\!\int f(\alpha_1,\alpha_2,\alpha_3)d\alpha_1 d\alpha_2 d\alpha_3, \tag{24}$$

and $|[x,y]|$ is the determinant of the secular equation for the waves with phases α_1, α_2, α_3. For a simple lattice one has

$$|[x,y]|=\begin{vmatrix}\sum_l\varphi_{xx}{}^l(e^{-i(l\alpha)}-1) & \sum_l\varphi_{xy}{}^l(e^{-i(l\alpha)}-1) & \sum_l\varphi_{xz}{}^l(e^{-i(l\alpha)}-1)\\ \sum_l\varphi_{yx}{}^l(e^{-i(l\alpha)}-1) & \text{——} & \text{——}\\ \sum_l\varphi_{zx}{}^l(e^{-i(l\alpha)}-1) & \text{——} & \text{——}\end{vmatrix} \tag{25}$$

where l is the index of the cell, representing really three integers l_1, l_2, l_3; $(l\alpha)=l_1\alpha_1+l_2\alpha_2+l_3\alpha_3$, and $\varphi_{xx}{}^l$, $\varphi_{xy}{}^l$, $\cdots$ the second derivatives of the potential energy between two lattice points in the relative position given by $l(l_1,l_2,l_3)$.

The determinant (25) can be written as a triple sum; one finds after some calculations:

$$|[x,y]|=64\sum_{(l>0)}\sum_{(l'>0)}\sum_{(l''>0)}\times\{ll'l''\}\sin^2\frac{(l\alpha)}{2}\sin^2\frac{(l'\alpha)}{2}\sin^2\frac{(l''\alpha)}{2}, \tag{26}$$

where $\sum_{(l>0)}$ indicates that the sum is to be extended only over half of the lattice points, in such a way that of two points l_1, l_2, l_3 and $-l_1, -l_2, -l_3$ one is to be omitted. The coefficient $\{ll'l''\}$ depends on the indices of 3 points, $l(l_1l_2l_3)$, $l'(l_1'l_2'l_3')$, $l''(l_1''l_2''l_3'')$, and can be written in such a way that it is expressed by the invariants of the distance vectors $\mathbf{r}^l$, $\mathbf{r}^{l'}$, $\mathbf{r}^{l''}$ of these three points (where $\mathbf{r}^l=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3$), namely $(\mathbf{r}^l)^2$, $(\mathbf{r}^{l''}\times\mathbf{r}^{l'})^2$ $(\mathbf{r}^l\cdot(\mathbf{r}^{l'}\times\mathbf{r}^{l''}))^2$. We introduce the operator

$$D=(1/r)(d/dr) \tag{27}$$

and write $[D\varphi(r)]_{r=r^l}=D\varphi^l$. Then we obtain:

$$\{ll'l''\}=D\varphi^l\cdot D\varphi^{l'}\cdot D\varphi^{l''}+(\mathbf{r}^l)^2D^2\varphi^l\cdot D\varphi^{l'}\cdot D\varphi^{l''}+\tfrac{1}{2}(\mathbf{r}^{l'}\times\mathbf{r}^{l''})^2\cdot D\varphi^l\cdot D^2\varphi^{l'}\cdot D^2\varphi^{l''}+\tfrac{1}{6}(\mathbf{r}^l\cdot(\mathbf{r}^{l'}\times\mathbf{r}^{l''}))^2\cdot D^2\varphi^l\cdot D^2\varphi^{l'}\cdot D^2\varphi^{l''}. \tag{28}$$

The invariants of the distance vectors depend only on the scalar products of the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, therefore, on account of (5), on the strain components x_x, $\cdots$ y_z, $\cdots$. Introducing (28) in (26) we get $|[x,y]|$ as a function of the x_x, $\cdots$ y_z, $\cdots$ and of α_1, α_2, α_3; averaging $\log|[x,y]|$ over these angles (as defined by (24)) leads to the value of $\bar{\omega}$, (23), as a function of x_x, $\cdots$ y_z, $\cdots$. This procedure, though quite definite and simple in principle, is in practice very involved and leads to formidable integrals. Therefore I shall use here a rather rough approximation, which is sufficient to show that our theory represents the main features of lattice thermodynamics.

[13] See, for instance, M. Born, *Atomtheorie des festen Zustandes* (Leipzig, 1923), p. 677. The method used here is due to O. Stern, Ann. d. Physik (4), **51**, 237 (1916).

If we assume $\varphi(r)$ as a power series in $1/r$, beginning with r^{-m} where the exponent m is large, we see that in the neighborhood of the minimum of φ the higher derivatives of φ will predominate. We proceed on the assumption that we can omit in (28) all terms except the last one which contains the highest derivatives and is proportional to the square of the volume of the parallelepiped determined by three lattice points:

$$\{ll'l''\} \backsimeq \tfrac{1}{6}(\mathbf{r}^{l}\cdot(\mathbf{r}^{l'}\times\mathbf{r}^{l''}))^2\cdot D^2\varphi^{l}\cdot D^2\varphi^{l'}\cdot D^2\varphi^{l''}. \quad (29)$$

We assume further that the potential $\varphi(r)$ decreases so quickly with the distance that only the few next neighbors have to be taken into account. We shall—rather arbitrarily—take the first and second neighbors in the static terms (Φ_0), but only the first neighbors in the vibrational terms ($\bar{\omega}$).

Finally, to fix our ideas, we consider one special case of a cubic lattice. The simple lattice is statically unstable if only the first neighbors are effective, and becomes stabilized only by the action of the second neighbors; this is the reason why this type practically never occurs in nature. The body-centered and the face-centered lattices occur in nature. I have decided (rather unfortunately, as was found later) to perform the calculations for the *body-centered lattice* since it has the coordination number 8 (instead of 12 for the face-centered lattice), and this number of the first neighbors determines the number of terms in the sum (26).

Then one obtains after some calculation

$$|[x,y]| = 64\times 16\,|\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3|^2\cdot(A_1R_1+A_2R_2+A_3R_3+A_4R_4), \quad (30)$$

where $A_\varkappa$, $R_\varkappa$ have the following meaning: The distances and phases for 4 of the 8 neighbors are:

$$\begin{aligned} l=1(1\,1\,1) &\qquad r_1=a_1+a_2+a_3\\ 2(-1\,1\,1) &\qquad r_2=-a_1+a_2+a_3\\ 3(1\,-1\,1) &\qquad r_3=a_1-a_2+a_3\\ 4(1\,1\,-1) &\qquad r_4=a_1+a_2-a_3 \end{aligned} \quad (31)$$

$$\begin{aligned} (1,\alpha)&=\alpha_1+\alpha_2+\alpha_3,\\ (2,\alpha)&=-\alpha_1+\alpha_2+\alpha_3,\\ (3,\alpha)&=\alpha_1-\alpha_2+\alpha_3,\\ (4,\alpha)&=\alpha_1+\alpha_2-\alpha_3. \end{aligned}$$

Then

$$\begin{aligned} A_1&=\sin^2\frac{(2,\alpha)}{2}\sin^2\frac{(3,\alpha)}{2}\sin^2\frac{(4,\alpha)}{2}, & R_1&=D^2\varphi_2\cdot D^2\varphi_3\cdot D^2\varphi_4,\\ A_2&=\sin^2\frac{(3,\alpha)}{2}\sin^2\frac{(4,\alpha)}{2}\sin^2\frac{(1,\alpha)}{2}, & R_2&=D^2\varphi_3\cdot D^2\varphi_4\cdot D^2\varphi_1,\\ A_3&=\sin^2\frac{(4,\alpha)}{2}\sin^2\frac{(1,\alpha)}{2}\sin^2\frac{(2,\alpha)}{2}, & R_3&=D^2\varphi_4\cdot D^2\varphi_1\cdot D^2\varphi_2,\\ A_4&=\sin^2\frac{(1,\alpha)}{2}\sin^2\frac{(2,\alpha)}{2}\sin^2\frac{(3,\alpha)}{2}, & R_4&=D^2\varphi_1\cdot D^2\varphi_2\cdot D^2\varphi_3, \end{aligned} \quad (32)$$

where $D^2\varphi_1=D^2\varphi(r_1)$ etc.

The functions $R_\varkappa$ have to be developed with respect to the $x_x,\ \cdots\ y_z,\ \cdots$. For this purpose it is convenient to use the fact that any function of the distance, $f(r)$, in which r is replaced by $(r^2+2\rho)^{\frac{1}{2}}$, has the following development:

$$f(r^2+2\rho)^{\frac{1}{2}}=f(r)+Df(r)\cdot\rho+\tfrac{1}{2}D^2f(r)\cdot\rho^2+\cdots, \quad (33)$$

just as a Taylor series where differentiation is replaced by the operator D.

For the four neighbor points (31) we have $r_1=r_2=r_3=r_4=a\sqrt{3}$ where a is the smallest coordinate difference in the lattice. The changes of r^2 for a deformation $x_x,\ \cdots\ y_z,\ \cdots$ are

$$\begin{aligned} \rho_1&=a^2(x_x+y_y+z_z+y_z+z_x+x_y),\\ \rho_2&=a^2(x_x+y_y+z_z+y_z-z_x-x_y),\\ \rho_3&=a^2(x_x+y_y+z_z-y_z+z_x-x_y),\\ \rho_4&=a^2(x_x+y_y+z_z-y_z-z_x+x_y). \end{aligned} \quad (34)$$

With the help of (33) and (34) it is easy to develop the $R_\varkappa$. The square of the determinant $|\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3|$ is equal to the determinant of the scalar products $\mathbf{a}_r\cdot\mathbf{a}_s$ and hence is expressible by the $x_x,\ \cdots\ y_z,\ \cdots$; one obtains for the terms up to the second order

$$|\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3|=a^3\{1+(x_x+y_y+z_z)-(y_z^2+z_z^2+x_y^2)+(y_yz_z+z_zx_x+x_xy_y)+\cdots\}. \quad (35)$$

These developments must be substituted in (30) and then the averaging performed, as prescribed

in (23). We omit the very lengthy calculations and write down only the result:*

$$f_0 = 4\varphi_3 + 3\varphi_4 + 3kT\{\tfrac{1}{2}\log(D^2\varphi_3) - \log T + \log a + C\},$$

$$f_1 = -\gamma a^3 p = 4a^2 D\varphi_3 + 4a^2 D\varphi_4 + kT\left(1 + \tfrac{3}{2}a^2\frac{D^3\varphi_3}{D^2\varphi_3}\right),$$

$$f_{11} = \gamma a^3 c_{11} = 4a^4 D^2\varphi_3 + 16a^4 D^2\varphi_4 + kT\left\{-2 + \tfrac{3}{2}a^4\left[\frac{D^4\varphi_3}{D^2\varphi_3} - \left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right]\right\},$$

$$f_{12} = \gamma a^3 c_{12} = 4a^4 D^2\varphi_3 + kT\cdot\tfrac{3}{2}a^4\left[\frac{D^4\varphi_3}{D^2\varphi_3} - \left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right],$$

$$f_{44} = \gamma a^3 c_{44} = 4a^4 D^2\varphi_3 + kT\left\{-1 + \tfrac{3}{2}a^4\left[\frac{D^4\varphi_3}{D^2\varphi_3} - \frac{16I_2+5}{9}\left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right]\right\},$$

where the constant C is given by

$$C = \log\frac{2^{5/3}\hbar I_0^{1/6}}{k\mu^{\frac{1}{2}}}. \tag{36a}$$

Here the lower indices, as in φ_3, φ_4, $D\varphi_3$ etc., indicate the square of the distance (in units a) for which the function is to be taken, e.g.

$$\varphi_3 = \varphi(a\sqrt{3}), \quad \varphi_4 = \varphi(a\sqrt{4}), \qquad D\varphi_3 = \frac{1}{a\sqrt{3}}\frac{\partial\varphi(a\sqrt{3})}{\partial a\sqrt{3}}, \quad \cdots. \tag{37}$$

According to our convention we have taken the first and second neighbors for the static terms, the first only for the kinetic terms.

In these expressions some numerical integrals appear, I_0 and I_2. As I_0 is only contained in the constant C its value is of no interest. The other constant is

$$I_2 = \frac{1}{(2\pi)^3}\int_{-\pi}^{+\pi}\!\!\int\!\!\int \frac{A_1^2}{(A_1+A_2+A_3+A_4)^2}\,d\alpha_1 d\alpha_2 d\alpha_3. \tag{38}$$

I have not succeeded† in finding an accurate value of I_2; but it is easy to see that it lies between $\frac{1}{16}$ and $\frac{1}{4}$. We shall write

$$I_2 = \tfrac{1}{4} - \epsilon, \quad \text{where} \quad 0 < \epsilon < \tfrac{3}{16}. \tag{38a}$$

One can check the long calculations with the help of the formulae (13a) which are indeed satisfied (observe the meaning of $D\varphi_3$, $D\varphi_4$ $\cdots$ etc. as explained in (37)).

The last step now consists in choosing a suitable function $\varphi(r)$. We take a law of the form

$$\varphi = u\frac{nm}{n-m}\left(-\frac{1}{m}\left(\frac{r_0}{r}\right)^m + \frac{1}{n}\left(\frac{r_0}{r}\right)^n\right), \tag{39}$$

then

$$\frac{d\varphi}{dr} = \frac{u}{r_0}\frac{nm}{n-m}\left(\left(\frac{r_0}{r}\right)^{m+1} - \left(\frac{r_0}{r}\right)^{n+1}\right)$$

vanishes for $r = r_0$; r_0 is therefore the equilibrium distance for two particles. The frequency ν_0 of vibration of one particle about this equilibrium, if the other particle is fixed, is given by

$$4\pi^2\mu\nu_0^2 = \left(\frac{d^2\varphi}{dr^2}\right)_{r=r_0} = \frac{u}{r_0^2}mn.$$

$u = -\varphi(r_0)$ is the *dissociation energy* of a molecule formed of two particles, which can also be expressed as a temperature $\Theta = u/k$. We introduce further instead of r_0 its projection a_0 on the cubic axes, given by $3a_0^2 = r_0^2$, and the corresponding volume $V_0 = N\gamma a_0^3$ which the crystal would have at zero temperature if only first neighbors interacted (the real volume at $T=0$ is a little smaller). We shall use further

* The formulae contain the well-known result that central forces, treated statically ($T=0$), lead to the Cauchy relation $c_{12}=c_{44}$; but they show at the same time that for $T>0$ this is not the case. This is worth noting as deviations from the Cauchy relation are usually considered as a criterion for noncentral forces which is not necessarily true.

† *Note added in proof.*—T. du Cros has found by numerical calculation that $I_2 = 1.85/16$, $\epsilon = 2.15/16$, for the body-centered lattice.

a quantity of the dimensions of pressure, $p_0 = R\Theta/V_0$, where $R = kN$ is the gas constant.

Our *law of force contains four constants*, the numbers m, n and any two of the quantities r_0 (or a_0, or V_0), ν_0, u, Θ, p_0, which are connected by

$$V_0 = N\gamma a_0^3 = N\gamma \frac{r_0^3}{3\sqrt{3}}, \quad u = k\Theta = \frac{4\pi^2}{mn}\mu\nu_0^2 r_0^2, \qquad p_0 V_0 = R\Theta. \tag{40}$$

We shall use a *final simplification* by choosing

$$n = 2m. \tag{41}$$

Lennard-Jones[14] has found this assumption successful in the theory of the virial coefficient of gases, for the special value $m = 6$, and he has used it also in his new order-disorder theory of melting, quoted above.

If we divide Eqs. (36) by $k\Theta$, the right-hand terms are dimensionless, independent of r_0. On the left-hand side the coefficient of $-p$, c_{11}, c_{12}, c_{44} becomes

$$\frac{\gamma a^3}{R\Theta} = \frac{\gamma a_0^3}{R\Theta}\frac{a^3}{a_0^3} = \frac{V_0}{R\Theta}\left(\frac{r}{r_0}\right)^3 = \frac{1}{p_0}\left(\frac{r}{r_0}\right)^3.$$

We choose now r_0 as unit of length and replace the variable $a = r/\sqrt{3}$ by

$$\xi = 1 - \frac{1}{r^m} = 1 - \left(\frac{1}{a\sqrt{3}}\right)^m. \tag{42}$$

Then the domain $1 \leqq r \leqq \infty$, extending from the equilibrium position of the first neighbors to infinity, corresponds to the range

$$0 \leqq \xi \leqq 1. \tag{42a}$$

As

$$\frac{1}{r^n} = \frac{1}{r^{2m}} = (1-\xi)^{2m}$$

φ and all derivatives, $D\varphi_3$, $D^2\varphi_3$, $\cdots$ $D\varphi_4$ $\cdots$ are polynomials in ξ; for instance

$$\frac{a^2}{u} D\varphi_3 = \frac{r^2}{3u} D\varphi(r) = \frac{2m}{3}(1-\xi)\cdot\xi.$$

The result of a long series of reductions is the following expressions:

$$\begin{aligned}
-\frac{p}{p_0}\frac{1}{(1-\xi)^{3/m}} &= F_1(\xi) + G_1(\xi) - \frac{T}{\Theta}H_1(\xi),\\
\frac{c_{11}}{p_0}\frac{1}{(1-\xi)^{3/m}} &= F_2(\xi) + G_2(\xi) - \frac{T}{\Theta}(2 + H_2(\xi)),\\
\frac{c_{12}}{p_0}\frac{1}{(1-\xi)^{3/m}} &= F_2(\xi) \qquad\qquad - \frac{T}{\Theta}H_2(\xi),\\
\frac{c_{44}}{p_0}\frac{1}{(1-\xi)^{3/m}} &= F_2(\xi)\\
&\quad - \frac{T}{\Theta}(1 + H_2(\xi) - 2H_3(\xi)),
\end{aligned} \tag{43}$$

where

$$F_1(\xi) = \frac{8m}{3}(1-\xi)\cdot\xi, \tag{44}$$

$$F_2(\xi) = \frac{8m^2}{9}(1-\xi)\cdot\left(1 - 2\frac{m+1}{m}\xi\right);$$

$$G_1(\xi) = 2\left(\tfrac{3}{4}\right)^{m/2} m^2 (1-\xi)\cdot\{1 - \left(\tfrac{3}{4}\right)^{m/2} + \left(\tfrac{3}{4}\right)^{m/2}\xi\},$$

$$\begin{aligned}
G_2(\xi) = 2\left(\tfrac{3}{4}\right)^{m/2} m^2 (1-\xi)&\\
\cdot\left\{1 - 2\frac{m+1}{m}\left[1 - \left(\tfrac{3}{4}\right)^{m/2}\right]\right.&\\
\left. - 2\frac{m+1}{m}\left(\tfrac{3}{4}\right)^{m/2}\xi\right\};&
\end{aligned} \tag{45}$$

$$H_1(\xi) = \frac{4+3m}{2}\,\frac{1 - \dfrac{4(m+1)^2}{m(3m+4)}\xi}{1 - 2\dfrac{m+1}{m}\xi},$$

$$H_2(\xi) = \frac{m^2-4}{3}\,\frac{\left(1 - \dfrac{m+1}{m}\xi\right)\cdot\left(1 + \dfrac{8(m+1)}{m(m-2)}\xi\right)}{\left(1 - 2\dfrac{m+1}{m}\xi\right)^2}, \tag{46}$$

$$H_3(\xi) = \frac{8(m+2)^2}{3}\left[\frac{1 - \dfrac{4}{3}\dfrac{m+1}{m}\xi}{1 - 2\dfrac{m+1}{m}\xi}\right]^2.$$

[14] J. E. Lennard-Jones, Physica (IV) **10**, 941 (1937).

TABLE I.*

ξ	$\sqrt{1-\xi}$	$F_1(\xi)$	$F_2(\xi)$	$G_1(\xi)$	$G_2(\xi)$	$H_1(\xi)$	$H_2(\xi)$	$H_3(\xi)$
−0.25	1.118	−5.00	63.3	2.99	−3.91	9.53	2.29	131
−0.20	1.095	−3.84	56.3	3.00	−5.54	9.73	3.26	136
−0.15	1.027	−2.76	49.7	3.00	−7.03	9.96	4.47	142
−0.10	1.049	−1.76	43.4	2.99	−8.37	10.24	6.00	150
−0.05	1.025	−0.84	37.5	2.96	−9.56	10.58	8.00	159
0	1.000	0	32.0	2.93	−10.60	11.00	10.67	171
0.05	0.975	0.76	26.9	2.88	−11.49	11.53	14.37	186
0.10	0.949	1.44	22.1	2.83	−12.23	12.22	19.72	207
0.15	0.922	2.04	17.7	2.76	−12.82	13.15	28.1	237
0.20	0.894	2.56	13.7	2.68	−13.26	14.50	42.2	285
0.25	0.866	3.00	10.0	2.59	−13.56	16.60	68.9	367
0.30	0.837	3.36	6.72	2.50	−13.70	20.33	131.0	539
0.35	0.806	3.64	3.81	2.39	−13.69	28.8	341.	1054
0.40	0.775	3.84	1.28	2.27	−13.54	67.0	2477.	5486
0.45	0.742	3.96	−0.88	2.14	−13.23	−73.0	4154.	6144

* I have to thank Dr. E. W. Kellermann for computing these tables and for helping me in the subsequent numerical work.

Table I contains the numerical values of these functions for $m=6$; this value corresponds to London's quantum-mechanical explanation of van der Waals force and has been successfully used by Lennard-Jones, as mentioned above.

The functions F_1, F_2 represent the statical effect of the first neighbors; G_1, G_2 that of the second neighbors. As G_1 is not small compared with F_1 the omission of all the more distant neighbors seems rather doubtful. Further, G_2 is negative, therefore c_{11} is smaller than c_{12} and c_{44} (at least for $T=0$, but really, as we shall see, throughout). Here it turns out that the choice of the body-centered lattice is unfortunate; for $c_{11}<c_{12}$ means instability (of the type leading to a "gel" state). In fact, one sees without calculation that for central forces acting only between first and second neighbors the face-centered lattice (densest packing) will be the most stable arrangement.*

I have, nevertheless, calculated graphs for all physical quantities. (We may assume that the stability with respect to the condition $c_{11}>c_{12}$ is maintained by other forces, not taken into account.) We shall concentrate our attention on c_{44} and investigate whether our thesis that $c_{44}=0$ means melting gives reasonable results.

It is easy to compute the quantities (43) as functions of p and T with the help of Table I, as the expressions (43) are linear in T/Θ. I have used a graphical method in which these linear functions are represented by straight lines; it is obviously sufficient to calculate two points of each line from the table. From these systems of straight lines (one for each of the quantities p, c_{11}, c_{12}, c_{44}) one can construct curves which give ξ (or the molar volume V) and the elastic constants as functions of p and T.

Figure 1 represents the isobars of thermic expansion, ξ (or V) for constant p as function of T/Θ. The V-scale is given in two forms; in the first one V is referred to V_0 as unit, the quantity used in the theoretical considerations (representing the volume of the lattice which it would have for $T=0$, $p=0$ if only the first neighbors interact); in the second scale V is referred to $V(0)$, the actual (calculated) volume for $T=0$, $p=0$. The figure shows that ξ increases first linearly with T/Θ, but later much quicker, until the increase becomes infinite. This extreme point is, of course, the absolute limit of stability; we have, nevertheless, continued the curves as dotted lines beyond these points.

Figure 2 shows the effect of compression with the help of some isotherms ξ (or V) as function of p/p_0.

Figures 3, 4, 5 and 6 represent the elasticity constants as functions of T/Θ for different hydrostatic pressures. As I could not determine the real value of the integral ϵ I have calculated c_{44} for two values of ϵ, namely $\epsilon=0$ (the lower limit) and $\epsilon=\frac{1}{16}$, which presumably is not far from the correct value. All constants decrease first linearly with T/Θ, but turn downward at last and reach the zero line at steep angles; the values of T/Θ where c_{44} vanishes should be the melting points for different pressures. We see that the behavior of the curves for c_{44} is rather different for $\epsilon=0$ and $\epsilon=\frac{1}{16}$; in the latter case, Fig. 6, the zero points of c_{44} are not the maximum values reached by T/Θ on the curves.

There is an arc on every curve on which to each value of c_{44}/p_0 there belong two values of T/Θ—a feature which could not well be foreseen from the general formulae (36). Those parts of the curves where c_{44} is not unique correspond apparently not to stable states of the lattices (or at least only to metastable, "overheated" states). The value of c_{44} jumps by a finite amount to zero at the melting point. Fig. 7 represents the melting curve $p(T)$, as taken from the zero points of c_{44} for $\epsilon=0$ and $\epsilon=\frac{1}{16}$; they do not differ much, but the latter is probably nearer to the truth. We see a slight increase of melting temperature with pressure.

* The calculation for the face-centered lattice will be performed by my collaborator, Mr. Teissier du Cros.

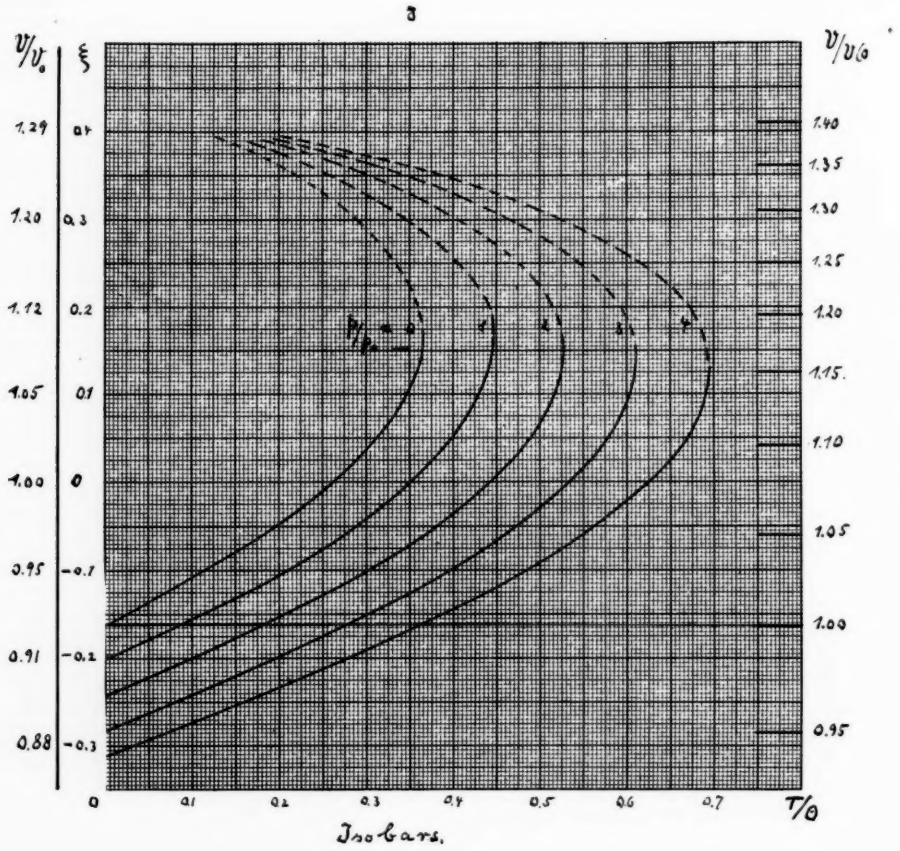

FIG. 1.

If we now compare the curves of c_{11}, c_{12}, c_{44} and particularly the zero points on them, we see that the curves of c_{12} and c_{44}, for $\epsilon=0$, practically coincide. The c_{11} curves lie lower and are flatter; this, as we have said already, is a consequence of the fact that the body-centered lattice is not the densest packing.

We have now to consider whether the order of magnitude is right. This depends on the values of Θ and p_0.

We introduce in (40)

$$m=\frac{n}{2}=6, \quad \gamma=4, \quad V_0=N\gamma a_0{}^3=\frac{N\gamma r_0{}^3}{3\sqrt{3}}, \quad M=\mu N;$$

then we get the dissociation energy u for a pair of particles in the form

$$D=Nu=R\Theta=\frac{\pi^2}{6\sqrt[3]{16}}\nu_0{}^2M\left(\frac{V_0}{N}\right)^{\frac{2}{3}}. \qquad (47)$$

If we express this in kcal, we find with $R=2$ cal.

$$\Theta=D\cdot 500°, \quad p_0=\frac{D}{V_0}\cdot 41{,}400 \text{ atmos.} \qquad (48)$$

For $D=5$, $V_0=20$ e.g. we have $\Theta=2500°$,

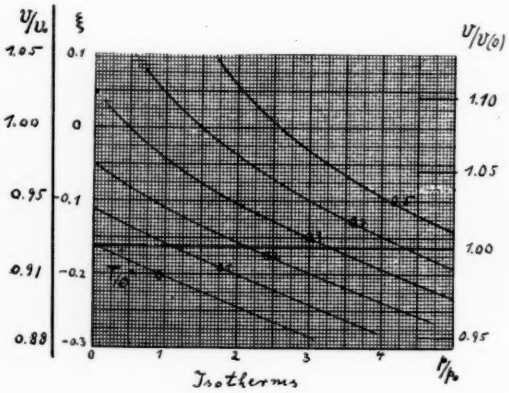

FIG. 2.

$p_0 = 10{,}000$ atmos. Our scale therefore covers the domain of high pressures investigated by Bridgman.

Figure 7 gives the melting point T_m as some numerical fraction of Θ for each value of p, say

$$T_m = \alpha\Theta. \tag{49}$$

Introducing this in (47) and solving with respect to ν_0 we get

$$\nu_0 = CR^{\frac{1}{2}}N^{\frac{1}{2}}(T_m/M)^{\frac{1}{2}}V_0^{-\frac{1}{3}}$$
$$= C\times 0.77\times 10^{12}(T_m/MV_0^{\frac{2}{3}})^{\frac{1}{2}}; \tag{50}$$

if we take for α the value from Fig. 7 which corresponds to $p=0$, $\alpha=0.35$, we obtain

$$C = \frac{1}{\pi}\left(\frac{6\cdot 4^{\frac{2}{3}}}{\alpha}\right)^{\frac{1}{2}} = 2.10. \tag{51}$$

The expression (50) is Lindemann's well-known formula with a definite numerical constant. Lindemann's empirical value is $C=2.75$; it is derived from those frequencies which allow the representation of specific heat with the help of Einstein's formula. Our ν_0 cannot be directly considered as a vibration of the lattice.

One can calculate the Debye frequency

$$\nu_D = c_m(3N/4\pi V)^{\frac{1}{3}}, \tag{52}$$

where c_m is a mean velocity of sound, from the theoretical expressions of c_{11}, c_{12}, c_{44}; but as the Debye formula of specific heat is valid only for deep temperatures, this calculation has nothing to do with our theory which is concerned with high temperatures (and pressures). I shall only show that ν_D differs from ν_0 only by a numerical factor. As c_{11}, c_{12}, c_{44} are proportional to p_0 we

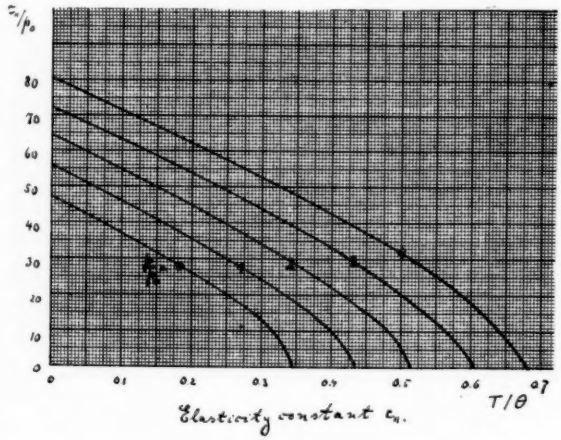

FIG. 3.

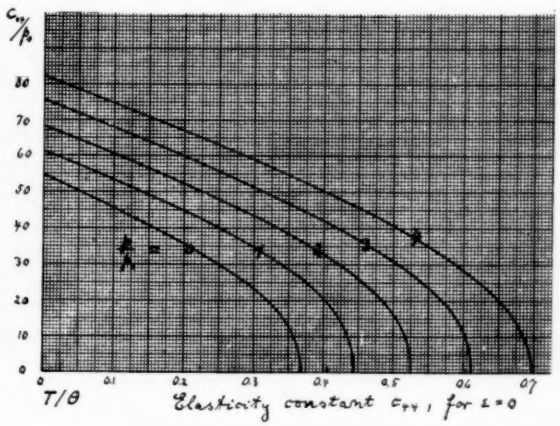

FIG. 5.

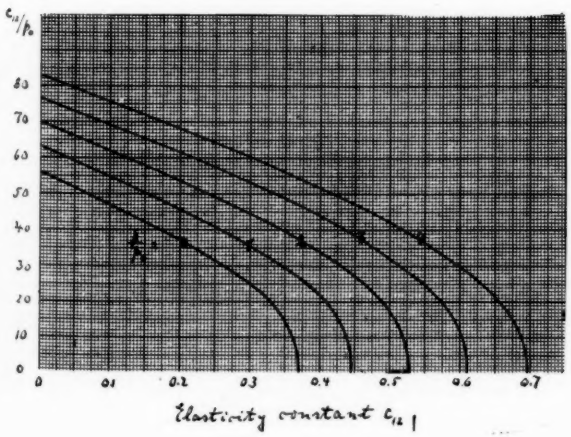

FIG. 4.

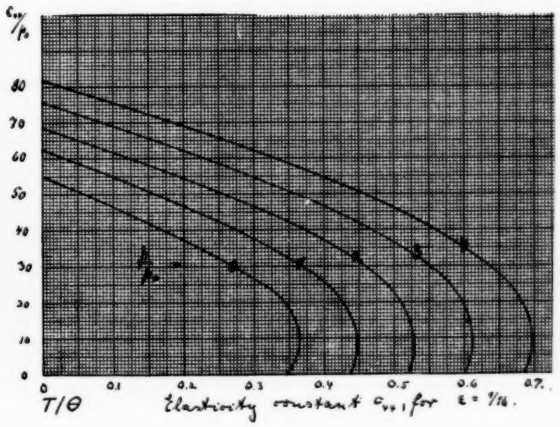

FIG. 6.

have

$$\rho c_m^2 = \beta p_0, \tag{53}$$

where ρ is the density and β a numerical factor. Now $\rho = M/V$ which we can replace by M/V_0 (since, according to Fig. 1, $V/V_0 = 0.93$ for $T = 0$). Then we have with the help of (47)

$$c_m^2 = \beta V_0 p_0 / M = \beta R\Theta / M = (\pi^2\beta/6\sqrt[3]{16})\nu_0^2 (V_0/N)^{\frac{2}{3}},$$

hence

$$\nu_D = 0.50\beta^{\frac{1}{2}} \cdot \nu_0. \tag{54}$$

All numerical values calculated in this paper are valid only for lattices of the body-centered cubic type and for the assumed law of force with $m = n/2 = 6$; for substances of this kind a "law of corresponding states" holds with respect to p and T if these are expressed as multiples of p_0 and Θ. I shall illustrate this by a remark about the latent heat of melting which, as we have said, cannot be calculated from the theory, since the change of volume depends on the properties of the liquid state. But if ΔV is given we can apply the Clausius-Clapeyron formula

$$Q = T(dp/dT)\Delta V$$

and take dp/dT from Fig. 7. We find

$$dp/dT = 11.1 p_0/\Theta = 11.1 R/V_0,$$
$$Q = 11.1(\Delta V/V_0)RT_m = 32. \tag{55}$$

The latent heat is proportional to the melting temperature and to $\Delta V/V$ with a numerical

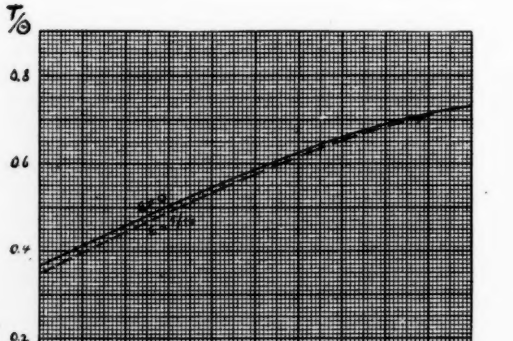

FIG. 7.

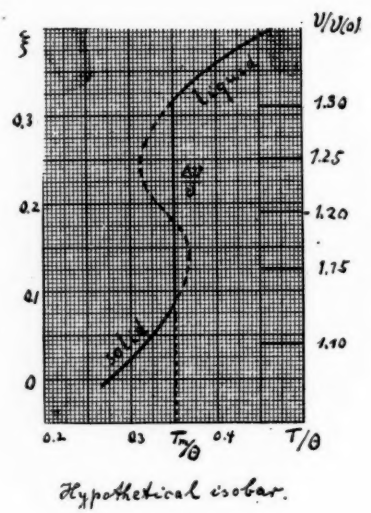

FIG. 8.

factor depending only on the lattice type and the exponent m.

I wish to make a final, quite hypothetical remark; it concerns the dotted parts of the expansion curves of Fig. 1. They represent completely unstable states of the lattice; but it can be expected that a more perfect theory which takes account of the disordered state of the liquid (as the theory of Lennard-Jones) will modify this part of the curves in the way indicated in Fig. 8. The ordinate of the melting point would intersect the curve in three points; the middle one would not represent a stable state, but the highest intersection point would correspond to the liquid in equilibrium with the solid. The liquid state would be represented by the continuation of the curve, exactly as in van der Waals theory of condensation. The existence of a critical point between liquid and solid seems therefore not impossible.

I expect that the method explained in this paper, properly improved, will be capable of accounting for the properties of strength, sliding and breaking of crystals. We have only to treat another stress component in the same way as we have here done with the pressure; we have to calculate the limit of stability with increasing temperature for a finite stress X_x (breaking) or X_y (sliding). This kind of problem is of special interest in connection with Bridgman's experimental investigations on breaking strength.

Bridgman has also discovered numerous allotropic transformations under high pressure; it will be interesting to see whether these can be accounted for by comparing the free energy of different lattices.

Metals need a special treatment as the forces arising from the free electrons are not central.

The extension of the theory to higher and deeper temperatures (anharmonic vibrations giving terms with T^2, quantum effects terms with $1/T$) will also be considered.

A complete account of the calculations will be published in collaboration with Dr. R. Schlapp. I have to thank him and Dr. K. Fuchs for valuable assistance in discussing the problems and checking the calculations, and Dr. E. W. Kellermann for computing the numerical table.

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The Equation of State of Frozen Neon, Argon, Krypton, and Xenon*

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(Received May 17, 1939)

The interaction between two rare gas atoms is assumed to have the form $-Ar^{-6}+AB(\exp^{-r/\rho})$. The values of A and B are found from the lattice distances and the heats of sublimation of frozen neon, argon, krypton and xenon for $\rho=0.2091$A and $\rho=0.345$A. The equations of state of the solids are then calculated, including the Debye θ's and the breakdown points, which occur a few degrees below the melting points. For krypton, the expansion coefficient and the specific heat are calculated, but are found too high at higher temperatures.

BY means of the crystal lattice theory and thermodynamics, it is possible to determine theoretically the structure and properties of matter from the potential energy of molecular interaction. The potential energy of interaction between pairs of particles may be divided into a repulsive and an attractive part. According to the quantum theory, the former has the form $be^{-r/\rho}$ for helium and neon. For other atoms or ions, there is good reason to assume the same form, but the value of the constants b and ρ is unknown; and even for helium and neon, it is not certain how far the necessary mathematical approximations have affected the calculated values. The Coulomb energy of attraction between ionic charges, which is proportional to $-e^2/r$, had first to be considered alone for ionic crystals, to which the theory was first applied. It turned out, however, that the van der Waals attraction, of the form $-A_1r^{-6}-A_2r^{-8}$, had also to be taken into account. Here again approximation formulae were available for the A's, but different methods of approximation gave different values. It seemed therefore advisable to take from the theory only the form of the energy expression and to leave the constants A, b, ρ, etc., to be determined from experiment.

Since the van der Waals attraction plays a minor role in the determination of lattice distance and lattice energy, A cannot be determined from the experimental data on these quantities. On the other hand, the van der Waals energy is extremely important for the calculation of the elastic properties. If a large number of suitably selected properties of the solid were known with great accuracy, it would be possible to determine the coefficients of the potential energy function from the measurements, but even then the calculations would be very complex.

One can hope that the situation is simpler for the rare gases. In the absence of charges, $-Ar^{-6}$ is the first term in the potential energy of attraction and one may assume as a first approximation this single type of attraction (the van der Waals attraction due to dipole-dipole interaction) and a single type of repulsion (that due to overlap of electron clouds). If the equilibrium distance between two atoms and the depth of

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the potential energy well are known, the coefficients of these two energy terms may be found. From this potential energy expression, it is possible to determine the equation of state for the solid and the gas. Obviously, any satisfactory theory must satisfy both of these states simultaneously.

The equation of state of solid argon has been treated according to this method by Herzfeld and Goeppert-Mayer.[1] Buckingham has examined the classical equation of state of gaseous helium, neon, and argon.[2]

This paper follows the method used by Herzfeld and Goeppert-Mayer.[1] The constants of the potential energy between two atoms were calculated from the lattice distance and the heat of sublimation at absolute zero. Using these constants, the equation of state in the solid form was determined. The calculations were made for neon, krypton, and xenon; the constants for argon were recalculated.[3]

Energy, Elastic Constants, and Frequency in a Face-Centered Cubic Lattice

The potential energy between two atoms of a rare gas may be represented by the equation

$$\varphi = -Ar^{-6} + ABe^{-r/\rho}, \tag{1}$$

where the first term is the van der Waals energy of attraction and the second, the energy of repulsion.

In the solid state, the energy necessary to remove an atom from a face-centered cubic crystal to an infinite distance is

$$\begin{aligned}\Phi = \Sigma\varphi = &-14.4539Ar^{-6} \\ &+12ABe^{-r/\rho}\times(1+\tfrac{1}{2}\exp(-(\sqrt{2}-1)r/\rho) \\ &+2\exp(-(3^{\frac{1}{2}}-1)r/\rho)+\exp(-(4^{\frac{1}{2}}-1)r/\rho) \\ &+4/3\exp(-(5^{\frac{1}{2}}-1)r/\rho)).\end{aligned} \tag{2}$$

These coefficients are obtained by summing up the contributions due to all the atoms of the crystal.[4] It is assumed that even in the crystal, the atoms interact by pairs.[5] The influence of the repulsive energy is small beyond the nearest neighbors but the attractive energy extends considerably farther and has a coefficient of almost $14\frac{1}{2}$ as compared to a factor slightly over 12 for the repulsive term.

The total energy of the crystal at absolute zero is

$$-U = N\Phi/2 + \tfrac{3}{2}Nh\bar{\nu}. \tag{3}$$

U is the heat of sublimation at absolute zero, $N\Phi/2$ the potential energy, and $\frac{3}{2}Nh\bar{\nu}$ the zero point energy. The average $\bar{\nu}$ used here is $\frac{3}{4}$ of the maximum ν of the Debye spectrum; so that

$$\tfrac{3}{2}Nh\bar{\nu} = 9/8Nh\nu \quad \text{and} \quad -U = +N\Phi/2 + 9/8R\theta \tag{3'}$$

θ is the Debye characteristic temperature.

The frequency is calculated from the elastic constants. For a cubic crystal, only three of these are distinct; *viz.*, c_{11}, c_{12}, and c_{44}. For a face-centered cubic lattice these are defined by the following equations.[1]

$$\begin{aligned}c_{11} = \frac{NA}{V}\Bigg\{ &B\frac{r^2+r\rho}{\rho^2}\exp(-r/\rho) \\ &\times\Bigg[1+\frac{2r+\sqrt{2}\rho}{r+\rho}\exp(-(\sqrt{2}-1)r/\rho) \\ &+2\frac{3r+3^{\frac{1}{2}}\rho}{r+\rho}\exp(-(3^{\frac{1}{2}}-1)r/\rho) \\ &+\frac{4r+4^{\frac{1}{2}}\rho}{r+\rho}\exp(-(4^{\frac{1}{2}}-1)r/\rho)+\cdots\Bigg] \\ &-\frac{24\times 2.544}{r^6}\Bigg\}+\frac{d}{dV}\left(\frac{N\Phi}{2}\right),\end{aligned} \tag{4}$$

$$\begin{aligned}c_{12} = \frac{NA}{V}\Bigg\{ &\frac{B}{2}\frac{r^2+r\rho}{\rho^2}\exp(-r/\rho) \\ &\times\Bigg[1+2\frac{3r+3^{\frac{1}{2}}\rho}{r+\rho}\exp(-(3^{\frac{1}{2}}-1)r/\rho) \\ &+\tfrac{1}{2}\frac{4r+4^{\frac{1}{2}}\rho}{r+\rho}\exp(-(4^{\frac{1}{2}}-1)r/\rho)+\cdots\Bigg] \\ &-\frac{24\times 1.137}{r^6}\Bigg\},\end{aligned} \tag{5}$$

$$c_{44} = c_{12} + (d/dV)(N\Phi/2). \tag{6}$$

[1] K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934).

[2] R. A. Buckingham, Proc. Roy. Soc. **A168**, 264 (1938).

[3] The solid forms of these elements belong to the face-centered cubic system. Helium has a hexagonal lattice. W. H. Keesom and K. W. Taconis, Proc. Amsterdam **41**, 95 (1938); Comm. Leiden Nr. 250*e*.

[4] Summations for inverse sixth power made by E. Lennard-Jones and A. E. Ingham, Proc. Roy. Soc. **A107**, 636 (1925).

[5] The validity of this assumption for the attractive term has been proved by F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

TABLE I. *Lattice distances in angstrom units.*

		References
Neon		
4.52	5°	a
Argon		
5.40	20°	b
5.42	40°	c
Krypton		
5.59	20°	d
5.68	82°	e
5.69	89°	e
5.69	90°	e
Xenon		
6.24	88°	e
	Heats of Sublimation at 0°K	
Neon	448 cal./mole	Calculated by Keesom; private communication of K. Clusius.
Argon	1850 cal./mole	Calculated by author.
Krypton	2678 cal./mole	f
Xenon	3778 cal./mole	Calculated by author.

[a] W. H. Keesom, J. de Smedt and H. H. Mooy, Proc. Acad. Amsterdam **33**, 255 (1930), Comm. Leiden. Nr. 203 e.
[b] W. H. Keesom and J. de Smedt, Comm. Leiden. Nr. 178 b (1926).
[c] F. Simon and Cl. v. Simon, Zeits. f. Physik **25**, 160 (1924).
[d] W. H. Keesom, J. de Smedt and H. H. Mooy, Proc. Acad. Amsterdam **33**, 814•(1930), Comm. Leiden Nr. 209 d.
[e] B. Ruhemann and F. Simon, Zeits. f. physik. Chemie **B15**, 389 (1932).
[f] K. Clusius, A. Kruis and Konnertz, Ann. d. Physik **33**, 642 (1938).

The maximum frequency of the Debye spectrum is defined from the equation given by Försterling.[6]

$$\nu^6 = V(9N^2/16\pi^2M^3)\{c_{11}c_{44}^2 + \tfrac{1}{5}c_{44}[(c_{11}-c_{44})^2-(c_{12}+c_{44})^2] + 1/105[(c_{11}-c_{44})^3-3(c_{11}-c_{44})(c_{12}+c_{44})^2 + 2(c_{12}+c_{44})^3]\}. \quad (7)$$

This differs from the formula used by Herzfeld and Goeppert-Mayer,[1] which is correct only when $c_{12}=c_{44}$.

In the formulae given for potential energy, elastic constants, and frequency there are three constants to be fixed; *viz.*, A, B, and ρ. Two values of ρ were assumed. The value $\rho=0.2091$A was deduced theoretically by Bleick and Mayer[7] for the interaction of two neon atoms. The value $\rho=0.345$A was found most suitable by Born and Mayer for alkali-halide crystals.[8] Using the above ρ's, those values of A and B were calculated which give the correct lattice distances and make the expression for total energy fit the experimental data for the heats of sublimation at absolute zero. (See Table I.)

For argon the lattice distance measured at 40° has been used. For xenon, an extrapolation was made to 0° by comparison with the expansion of krypton.[9] The distance between the nearest neighbors equals the lattice distance divided by $\sqrt{2}$. The heats of sublimation at absolute zero were calculated from the measurements of

[6] K. Försterling, Ann. d. Physik. **4**, 549 (1920).
[7] W. E. Bleick and J. E. Mayer. J. Chem. Phys. **2**, 252 (1934). The derivation of this value has been criticized by Buckingham, reference 2.

TABLE II. *Constants of potential energy function.* Na *in ergs* cm^6 *and* B *in* cm^{-6}, ρ *in A.*

	ρ	Na$\times10^{35}$	B$\times10^{-48}$
Neon	0.2091	0.4861	1270
	0.345	0.8447	6.9
Argon	0.2091	5.265	9500
	0.250	5.782	596
	0.300	6.631	57.6
	0.345	7.555	12.8
Krypton	0.2091	8.924	14700
	0.345	12.615	15.0
Xenon	0.2091	21.336	52000
	0.345	28.720	24.6

TABLE III (a).

	Neon	Argon	Krypton	Xenon
		$\rho=0.2091A$		
$C_1\times10^{60}$	7.97	69.5	129	273
$A\times10^{60}$	8.07	87.4	148	354
		$\rho=0.345A$		
$C_1\times10^{60}$	7.97	69.5	129	273
$A\times10^{60}$	14.0	125	209	477

TABLE III (b). *Krypton* ($\rho=0.345A$).

$\varphi=-(A_1r^{-6}+A_2r^{-8})+A_1Be^{-r/\rho}$			
$C_1\times10^{60}$	136	$C_2\times10^{76}$	420
$A_1\times10^{60}$	190	$A_2\times10^{76}$	587
B	18.7		

[8] M. Born and J. E. Mayer. Zeits. f. Physik. **75**, 1 (1932).
[9] The method of extrapolation was kindly suggested by Professor Lennard-Jones. It was assumed that the total relative expansion from zero degrees absolute to the melting point was the same for krypton and xenon and that at those temperatures which were in the same ratio as the melting points, both had the same relative expansion.

Clusius[10] on heats of vaporization and specific heats at constant pressure. The value of 1655 cal./mole for argon used by Herzfeld and Goeppert-Mayer is too low as has been noted by Buckingham.[2] For this reason, the constants for this gas have been recalculated, using the value 1850 cal./mole. A method of successive approximations leads to the values of Na and B given in Table II ($N=6.022\times10^{23}$). In Table III(a) the

[10] K. Clusius. Zeits. f. physik. Chemie **B31**, 459 (1936); K. Clusius and L. Riccoboni Zeits. f. physik Chemie **B38**, 81, (1937).

TABLE IV. *Frequency, elastic constants and energy r in A, energy in kilojoule, elastic constants in ergs/cm³, $\theta=h\nu/k$ in degrees Kelvin.*

				Neon; $\rho=0.2091A$					
r	3.05	3.10	3.15	3.20	3.22	3.24	3.25	3.26	3.27	3.28
θ	99.92	85.33	72.12	60.08	55.53	51.08	48.89	46.73	44.57	42.42
$c_{11}\times10^{-9}$	23.805	16.388	10.881	6.832	5.536	4.395	3.878	3.394	2.940	2.51
$c_{12}\times10^{-9}$	13.238	9.016	5.895	3.610	2.881	2.241	1.952	1.681	1.428	1.197
$c_{44}\times10^{-9}$	13.554	9.992	7.285	5.238	4.567	3.969	3.694	3.435	3.191	2.962
$-N\Phi/2$	2.648	2.608	2.533	2.435	2.391	2.346	2.322	2.299	2.275	2.250
$3/2\ Nh\ 3/4\nu$	0.934	0.798	0.675	0.562	0.519	0.478	0.457	0.437	0.417	0.390
$+U$	1.714	1.810	1.858	1.873	1.872	1.868	1.865	1.862	1.858	1.857
				Neon; $\rho=0.345A$					
r	3.05	3.10	3.15	3.20	3.25	3.30	3.35	3.40		
θ	69.31	63.53	58.00	52.71	47.65	42.77	38.33	32.30		
$c_{11}\times10^{-9}$	11.233	8.948	7.035	5.441	4.117	3.026	2.131	1.400		
$c_{12}\times10^{-9}$	6.951	5.548	4.372	3.392	2.578	1.905	1.354	0.903		
$c_{44}\times10^{-9}$	6.864	5.824	4.920	4.140	3.466	2.888	2.393	1.970		
$-N\Phi/2$	2.440	2.434	2.408	2.366	2.311	2.247	2.175	2.098		
$3/2\ Nh\ 3/4\nu$	0.648	0.594	0.542	0.493	0.446	0.400	0.359	0.302		
$+U$	1.792	1.840	1.866	1.873	1.865	1.847	1.816	1.796		
				Argon; $\rho=0.2091A$					
r	3.73	3.78	3.83	3.88	3.93	3.98	4.03	4.08		
θ	141.5	122.3	105.2	89.73	75.74	62.80	50.69	43.78		
$c_{11}\times10^{-10}$	8.064	5.817	4.118	2.838	1.881	1.168	0.6425	0.2598		
$c_{12}\times10^{-10}$	4.394	3.144	2.202	1.495	0.9676	0.5774	0.2916	0.0849		
$c_{44}\times10^{-10}$	4.227	3.170	2.360	1.739	1.267	0.9073	0.6347	0.4293		
$-N\Phi/2$	8.755	8.813	8.724	8.530	8.263	7.948	7.603	7.242		
$3/2\ Nh\ 3/4\nu$	1.323	1.144	0.984	0.839	0.708	0.587	0.474	0.409		
$+U$	7.432	7.669	7.740	7.691	7.555	7.361	7.129	6.833		
				Argon; $\rho=0.345A$					
r	3.73	3.78	3.83	3.88	3.93	3.98	4.03	4.08		
θ	97.16	88.59	80.55	72.98	65.88	59.10	52.67	46.50		
$c_{11}\times10^{-10}$	3.701	2.959	2.342	1.832	1.411	1.063	0.7778	0.5451		
$c_{12}\times10^{-10}$	2.182	1.741	1.374	1.071	0.8214	0.6159	0.4477	0.3106		
$c_{44}\times10^{-10}$	2.091	1.747	1.455	1.208	0.9994	0.8218	0.6729	0.5475		
$-N\Phi/2$	8.498	8.534	8.492	8.388	8.234	8.042	7.820	7.577		
$3/2\ Nh\ 3/4\nu$	0.909	0.829	0.753	0.683	0.616	0.553	0.493	0.435		
$+U$	7.589	7.705	7.739	7.705	7.618	7.489	7.327	7.142		
				Krypton; $\rho=0.2091A$					
r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20	4.25	
θ	121.3	105.5	91.12	78.16	66.45	55.77	45.89	36.49	26.82	
$c_{11}\times10^{-10}$	12.217	8.910	6.398	4.497	3.067	1.996	1.200	0.6146	0.1893	
$c_{12}\times10^{-10}$	6.585	4.817	3.428	2.380	1.594	1.009	0.5756	0.2590	0.0308	
$c_{44}\times10^{-10}$	6.209	4.730	3.541	2.629	1.931	1.399	0.9942	0.6879	0.4575	
$-N\Phi/2$	11.865	12.078	12.059	11.871	11.565	11.176	10.735	10.261	9.773	
$3/2\ Nh\ 3/4\nu$	1.135	0.987	0.852	0.731	0.622	0.522	0.429	0.341	0.251	
$+U$	10.730	11.091	11.207	11.140	10.943	10.654	10.306	9.920	9.522	
				Krypton; $\rho=0.345A$					
r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20		
θ	81.68	74.98	68.28	61.97	56.04	50.59	45.14	40.08		
$c_{11}\times10^{-10}$	5.442	4.372	3.485	2.748	2.139	1.635	1.220	0.8809		
$c_{12}\times10^{-10}$	3.094	2.555	2.031	1.596	1.236	0.9398	0.6965	0.4975		
$c_{41}\times10^{-10}$	2.904	2.504	2.088	1.735	1.437	1.184	0.9717	0.7926		
$-N\Phi/2$	11.739	11.851	11.845	11.744	11.565	11.329	11.045	10.727		
$3/2\ Nh\ 3/4\nu$	0.764	0.701	0.639	0.580	0.524	0.472	0.422	0.375		
$+U$	10.975	11.150	11.206	11.164	11.041	10.857	10.623	10.352		
				Xenon; $\rho=0.2091A$					
r	4.25	4.30	4.35	4.40	4.45	4.50	4.55	4.60	4.65	
θ	115.04	100.11	86.72	74.69	63.82	53.94	44.86	36.34	27.96	
$c_{11}\times10^{-10}$	14.698	10.816	7.854	5.600	3.891	2.604	1.639	0.922	0.394	
$c_{12}\times10^{-10}$	7.930	5.798	4.174	2.943	2.013	1.314	0.793	0.408	0.127	
$c_{44}\times10^{-10}$	7.476	5.658	4.257	3.179	2.351	1.717	1.233	0.865	0.58	
$-N\Phi/2$	16.253	16.589	16.614	16.412	16.048	15.571	15.017	14.416	13.796	
$3/2\ Nh\ 3/4\nu$	1.076	0.936	0.811	0.698	0.597	0.504	0.420	0.340	0.260	
$+U$	15.177	15.653	15.803	15.714	15.451	15.067	14.597	14.076	13.522	
				Xenon; $\rho=0.345A$					
r	4.25	4.30	4.35	4.40	4.45	4.50	4.55	4.60	4.65	
θ	78.53	71.75	65.39	59.42	53.82	48.53	43.55	38.80	34.27	
$c_{11}\times10^{-10}$	6.702	5.419	4.348	3.456	2.714	2.099	1.591	1.172	0.829	
$c_{12}\times10^{-10}$	3.857	3.108	2.484	1.965	1.534	1.178	0.884	0.643	0.446	
$c_{44}\times10^{-10}$	3.622	3.029	2.526	2.100	1.740	1.435	1.178	0.962	0.780	
$-N\Phi/2$	16.224	16.404	16.423	16.312	16.097	15.800	15.438	15.027	14.581	
$3/2\ Nh\ 3/4\nu$	0.735	0.671	0.612	0.556	0.503	0.454	0.407	0.363	0.321	
$+U$	15.489	15.733	15.811	15.756	15.594	15.346	15.031	14.664	14.260	

van der Waals coefficients of Table II are compared with those calculated theoretically by Slater and Kirkwood,[11] from the polarizability of the gases.

The numerical values obtained for the elastic constants, using Eqs. (4), (5) and (6), are given in Table IV.

In Fig. 1, interatomic distance is plotted against theoretical potential energy for neon ($\rho=0.345$A). This figure shows clearly how the zero point energy changes the total energy and shifts r_0, the minimum of total energy, to a different position from r_m, the minimum of potential energy. Table V shows both the lattice shift and the part the zero point energy plays in the total energy. This is small in the case of xenon, but rather large for neon. Using experimental values alone, Clusius[10] has shown that the zero point energy is 77 percent of the potential energy in helium. The value of $-N\Phi/2$ for r_m is not equal to $U+9/8R\theta$ at r_0. The reason for this is obvious from Fig. 1.

The shift from r_0 to r_m is the same for both values of ρ except in the case of neon. Even for neon, if one considers only the repulsion due to the twelve nearest neighbors, the shift is the same for both values of ρ. This fact is very useful in calculating A and B. From formula (2), it is

TABLE V. (*Energy in kj; distance in A*).

	NEON	ARGON	KRYPTON	XENON
		$\rho=0.2091A$		
r_0	3.20	3.83	3.95	4.35
r_m	3.03	3.78	3.92	4.33
$-\frac{N\Phi}{2}(r=r_m)$	2.65	8.81	12.11	16.64
$+U(r=r_0)$	1.87	7.74	11.21	15.81
$\frac{9/8R\theta}{U+9/8R\theta}(r=r_0)$	26.6%	11.3%	7.1%	4.9%
		$\rho=0.345A$		
r_0	3.20	3.83	3.95	4.35
r_m	3.06	3.78	3.92	4.33
$-\frac{N\Phi}{2}(r=r_m)$	2.44	8.53	11.86	16.43
$+U(r=r_0)$	1.87	7.74	11.21	15.81
$\frac{9/8R\theta}{U+9/8R\theta}(r=r_0)$	22.4%	8.9%	5.4%	3.7%

[11] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931). Cf. H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

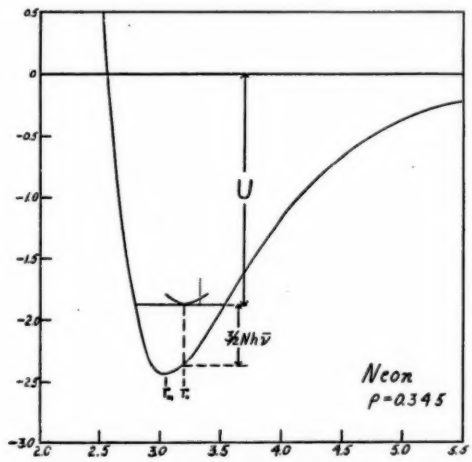

FIG. 1. Potential energy in kilojoules per mole as a function of interatomic distance in A for neon ($\rho=0.345$A). The value of $-U$ is plotted in the region calculated. The breakdown point at zero pressure, as indicated by the dotted line, is only a short distance from the equilibrium position at 0°.

evident that B is a unique function of r_m and ρ. Hence, when B has been found for one value of ρ, it is quite a simple matter to find it for other values of ρ. Likewise, A may be determined for a new value of ρ when two values are already known by making an interpolation for θ. For two additional ρ's, values of A, B, and θ have been calculated for argon ($\rho=0.250$A and $\rho=0.300$A). (See Tables II and VII.)

In Table VII are compared the values of θ obtained from formula (3′) with those calculated from the specific heat curves by Clusius. The values of θ obtained by using $\rho=0.345$A are in very good agreement with experiment except in the case of neon. The good agreement for neon where $\rho=0.2091$A might indicate that a different value of ρ should be used for each gas.[12]

EQUATION OF STATE

Using the data in Table IV, the equation of state of the crystal has been determined from the thermodynamic relation

$$p=-(\partial A/\partial V)_T. \tag{8}$$

This pressure is divided into three parts[1]

$$p_1=-\frac{\partial}{\partial V}\left(\frac{N\Phi}{2}\right), \quad (8') \qquad p_2=-\frac{\partial}{\partial V}(\tfrac{3}{2}Nh\bar{\nu}) \quad (8'')$$

[12] J. A. Wasastjerna, Roy. Soc. Phil. Trans., **237**, 105 (1938).

and $$p_3 = -E\partial 1n\nu/\partial V, \qquad (8''')$$

where

$$E = \int_0^T C_v dT \qquad (9)$$

p_1+p_2 give the pressure at 0° for any volume. p_3 is the thermal pressure which is added to the pressure at 0°. The results obtained are tabulated in Table VI. The isotherms for krypton are shown graphically in Fig. 2, ($\rho=0.2091$A), and by the continuous lines in Fig. 3, ($\rho=0.345$A). One may observe that the isotherms at higher temperatures have minima. A crystal whose pressure increases with volume is unstable; so we interpret a minimum on the curve as a breakdown point.

Herzfeld and Goeppert-Mayer[1] have made an attempt to find some relation between the melting points and the breakdown points at zero pressure.[13] In Fig. 3 this point occurs at 108°. Table VII compares the breakdown points at zero pressure with the melting points. The coincidence of values is quite remarkable for

[13] L. Brillouin has first suggested that the melting point may be the point where c_{44}, the resistance to shear, becomes zero. This would make c_{11} and c_{12} negative. Comptes rendus **192**, 668, (1931); cf. Phys. Rev. **54**, 916 (1938).

TABLE VI. *Pressure. V in cc, pressure in 10^8 dynes/cm², ν in 10^{12} sec.$^{-1}$.**

				Neon; $\rho=0.2091A$					
r	3.05	3.10	3.15	3.20	3.22	3.24	3.25	3.26	3.27	3.28
V	12.08	12.69	13.31	13.95	14.22	14.48	14.62	14.75	14.89	15.03
ν	2.107	1.799	1.521	1.267	1.171	1.077	1.031	0.985	0.940	0.894
$-\partial \ln \nu/\partial V$	0.258	0.260	0.270	0.291	0.304	0.321	0.330	0.341	0.354	0.368
p_1	−3.16	−9.76	−13.90	−16.28	−16.86	−17.27	−17.42	−17.54	−17.62	−17.68
p_2	24.08	20.76	18.19	16.32	15.79	15.32	15.09	14.90	14.74	14.59
0° p	*20.92*	*11.00*	*4.29*	*0.04*	*−1.07*	*−1.95*	*−2.33*	*−2.64*	*−2.88*	*−3.09*
4° p_3	0.003	0.007	0.010	0.017	0.022	0.029	0.035	0.040	0.050	0.059
p	*20.92*	*11.01*	*4.30*	*0.06*	*−1.05*	*−1.92*	*−2.29*	*−2.60*	*−2.83*	*−3.03*
8° p_3	0.05	0.08	0.15	0.24	0.33	0.42	0.49	0.57	0.66	0.76
p	*20.97*	*11.08*	*4.44*	*0.28*	*−0.74*	*−1.53*	*−1.84*	*−2.07*	*−2.22*	*−2.33*
12° p_3	0.26	0.39	0.62	1.02	1.26	1.43	1.75	1.95	2.18	2.45
p	*21.18*	*11.39*	*4.91*	*1.06*	*0.19*	*−0.52*	*−0.58*	*−0.69*	**−0.70**	*−0.64*
14° p_3	0.45	0.68	1.04	1.63	1.97	2.37	2.62	2.90	3.23	3.59
p	*21.37*	*11.68*	*5.33*	*1.67*	*0.90*	*0.42*	*0.29*	**0.26**	*0.35*	*0.50*
20° p_3	1.51	2.10	2.90	4.10	4.74	5.53	5.98	6.46	7.04	7.67
p	*22.43*	*13.10*	*7.19*	*4.14*	*3.67*	**3.58**	*3.65*	*3.82*	*4.16*	*4.58*
25° p_3	2.91	3.82	5.02	6.70	7.59	8.66	9.23	9.94	10.73	11.53
p	*23.83*	*14.83*	*9.31*	*6.74*	**6.52**	*6.71*	*6.90*	*7.30*	*7.86*	*8.42*
				Neon; $\rho=0.345A$					
r	3.05	3.10	3.15	3.20	3.25	3.30	3.35	3.40		
V	12.08	12.69	13.31	13.95	14.62	15.30	16.01	16.74		
ν	1.461	1.339	1.223	1.112	1.005	0.902	0.802	0.681		
$-\partial \ln \nu/\partial V$	0.143	0.144	0.147	0.150	0.154	0.160	0.174	0.243		
p_1	0.87	−2.76	−5.48	−7.48	−8.89	−9.83	−10.39	−10.67		
p_2	9.26	8.56	7.94	7.39	6.87	6.41	6.19	7.33		
0° p	*10.13*	*5.80*	*2.46*	*−0.09*	*−2.02*	*−3.42*	**−4.20**	*−3.34*		
16° p_3	0.90	1.06	1.25	1.49	1.77	2.16	2.82	4.10		
p	*11.03*	*6.86*	*3.71*	*1.40*	*−0.25*	*−1.26*	**−1.38**	*0.76*		
21° p_3	1.85	2.11	2.42	2.77	3.15	3.63	4.33	6.68		
p	*11.98*	*7.91*	*4.88*	*2.68*	*1.10*	*0.21*	**0.13**	*3.34*		
24° p_3	2.53	2.87	3.22	3.63	4.07	4.65	5.46	8.31		
p	*12.66*	*8.67*	*5.68*	*3.54*	*2.07*	**1.23**	*1.26*	*4.97*		
				Argon; $\rho=0.2091A$					
r	3.73	3.78	3.83	3.88	3.93	3.98	4.03			
V	22.098	22.999	23.923	24.873	25.847	26.846	27.870			
ν	2.983	2.580	2.219	1.893	1.597	1.324	1.069			
$-\partial \ln \nu/\partial V$	0.161	0.162	0.165	0.170	0.180	0.196	0.225			
p_1	16.75	−2.56	−15.76	−24.45	−29.98	−32.99	−34.31			
p_2	21.28	18.53	16.21	14.29	12.74	11.53	10.65			
0° p	*38.03*	*15.97*	*0.45*	*−10.16*	*−17.24*	*−21.46*	*−23.66*			
10° p_3	0.03	0.04	0.07	0.12	0.19	0.34	0.64			
p	*38.06*	*16.01*	*0.53*	*−10.04*	*−17.06*	*−21.12*	*−23.02*			
20° p_3	0.41	0.60	0.87	1.25	1.79	2.60	3.90			
p	*38.44*	*16.57*	*1.32*	*−8.91*	*−15.46*	*−18.86*	*−19.76*			
30° p_3	1.60	2.13	2.78	3.62	4.71	6.22	8.47			
p	*39.63*	*18.10*	*3.23*	*−6.54*	*−12.54*	*−15.24*	*−15.19*			
40° p_3	3.57	4.45	5.49	6.73	8.27	10.39	13.52			
p	*41.60*	*20.42*	*5.94*	*−3.43*	*−8.98*	**−11.07**	*−10.14*			
50° p_3	6.13	7.32	8.65	10.23	12.19	14.83	18.78			
p	*44.16*	*23.29*	*9.10*	*0.07*	*−5.06*	**−6.63**	*−4.88*			
60° p_3	9.07	10.41	12.09	13.95	16.27	19.42	24.15			
p	*47.10*	*26.38*	*12.54*	*3.79*	*−0.98*	**−2.04**	*0.49*			
65° p_3	10.56	12.17	13.90	15.87	18.35	21.76	26.85			
p	*48.59*	*28.14*	*14.35*	*5.71*	*1.10*	**0.30**	*3.19*			
70° p_3	11.88	13.90	15.71	17.81	20.46	24.10	29.57			
p	*49.91*	*29.87*	*16.16*	*7.65*	*3.21*	**2.64**	*5.91*			
80° p_3	15.63	17.45	19.43	21.76	24.72	28.82	35.04			
p	*53.66*	*33.42*	*19.88*	*11.60*	*7.47*	**7.36**	*11.38*			
84° p_3	17.02	18.90	20.94	23.37	26.45	30.72	37.25			
p	*55.05*	*34.87*	*21.39*	*13.21*	**9.20**	*9.26*	*13.59*			
90° p_3	19.14	21.09	23.23	25.79	29.04	33.57	40.55			
p	*57.17*	*37.06*	*23.68*	*15.63*	**11.79**	*12.11*	*16.89*			
100° p_3	22.74	24.81	27.10	29.84	33.37	38.37	46.06			
p	*60.77*	*40.78*	*27.55*	*19.68*	**16.12**	*16.91*	*22.40*			

* Total pressures are in italics; minimum pressures are in boldface type.

TABLE VI (*Continued*).

				Argon; ρ = 0.345A				
r	3.73	3.78	3.83	3.88	3.93	3.98	4.03	4.08
V	22.098	22.999	23.923	24.873	25.847	26.846	27.870	28.921
ν	2.049	1.868	1.698	1.539	1.389	1.246	1.111	0.981
$-\partial \ln \nu/\partial V$	0.103	0.103	0.103	0.105	0.107	0.110	0.115	0.122
p_1	9.10	−0.64	−8.07	−13.64	−17.80	−20.60	−22.52	−23.69
p_2	9.33	8.51	7.78	7.13	6.57	6.09	5.67	5.32
0° p	*18.43*	*7.87*	*−0.29*	*−6.51*	*−11.23*	*−14.51*	*−16.85*	*−18.37*
10° p_3	0.055	0.074	0.093	0.123	0.164	0.221	0.302	0.419
p	*18.49*	*7.94*	*−0.20*	*−6.39*	*−11.07*	*−14.29*	*−16.55*	*−17.95*
20° p_3	0.64	0.77	0.93	1.11	1.32	1.59	1.91	2.34
p	*19.07*	*8.64*	*0.64*	*−5.40*	*−9.91*	*−12.92*	*−14.94*	*−16.03*
30° p_3	1.95	2.22	2.52	2.85	3.28	3.69	4.22	4.90
p	*20.38*	*10.09*	*2.23*	*−3.66*	*−7.95*	*−10.82*	*−12.63*	*−13.47*
40° p_3	3.74	4.11	4.51	4.96	5.46	6.07	6.78	7.69
p	*22.17*	*11.98*	*4.22*	*−1.55*	*−5.77*	*−8.44*	*−10.07*	*−10.68*
50° p_3	5.78	6.23	6.71	7.25	7.85	8.58	9.47	10.59
p	*24.21*	*14.10*	*6.42*	*0.74*	*−3.38*	*−5.93*	*−7.38*	*−7.78*
60° p_3	7.98	8.48	9.02	9.63	10.33	11.18	12.21	13.53
p	*26.41*	*16.35*	*8.73*	*3.12*	*−0.90*	*−3.33*	*−4.64*	*−4.84*
70° p_3	10.27	10.81	11.41	12.08	12.86	13.82	14.99	16.50
p	*28.70*	*18.68*	*11.12*	*5.57*	*1.63*	*−0.69*	**−1.86**	**−1.87**
76° p_3	11.68	12.39	13.01	13.71	14.53	15.41	16.78	18.41
p	*30.11*	*20.26*	*12.72*	*7.20*	*3.30*	*0.90*	**−0.07**	*0.04*
80° p_3	12.62	13.21	13.84	14.58	15.42	16.47	17.79	19.50
p	*31.05*	*21.08*	*13.55*	*8.07*	*4.19*	*1.96*	**0.94**	*1.13*
84° p_3	13.57	14.17	14.83	15.58	16.45	17.53	18.91	20.69
p	*32.00*	*22.04*	*14.54*	*9.07*	*5.22*	*3.02*	**2.06**	*2.32*
90° p_3	15.03	15.63	16.31	17.08	18.00	19.14	20.60	22.50
p	*33.46*	*23.50*	*16.02*	*10.57*	*6.77*	*4.63*	**3.75**	*4.13*
100° p_3	17.46	18.09	18.78	19.61	20.59	21.84	23.42	25.52
p	*35.89*	*25.96*	*18.49*	*13.10*	*9.36*	*7.33*	**6.57**	*7.15*
				Krypton; ρ = 0.2091A				
r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20
V	24.300	25.259	26.243	27.252	28.287	29.348	30.435	31.548
ν	2.558	2.225	1.921	1.648	1.401	1.176	0.967	0.769
$-\partial \ln \nu/\partial V$	0.143	0.148	0.151	0.154	0.160	0.170	0.190	0.231
p_1	37.55	8.75	−11.31	−24.89	−33.70	−39.04	−41.86	−42.89
p_2	16.21	14.59	12.84	11.28	9.95	8.88	8.17	7.90
0° p	*53.76*	*23.34*	*1.53*	*−13.61*	*−23.75*	*−30.16*	*−33.69*	*−34.99*
20° p_3	0.54	0.77	1.08	1.46	1.96	2.64	3.68	5.48
p	*54.30*	*24.11*	*2.61*	*−12.15*	*−21.79*	*−27.52*	**−30.01**	*−29.51*
40° p_3	3.98	4.91	5.87	6.92	8.15	9.70	12.10	16.06
p	*57.74*	*28.25*	*7.40*	*−6.69*	*−15.60*	*−20.46*	**−21.59**	*−18.93*
60° p_3	9.34	10.82	12.24	13.73	15.43	17.67	21.16	27.34
p	*63.10*	*34.16*	*13.77*	*0.12*	*−8.32*	*−12.49*	**−12.53**	*−7.65*
80° p_3	15.52	17.46	19.36	21.02	23.07	25.87	30.44	38.70
p	*69.28*	*40.80*	*20.89*	*7.41*	*−0.68*	**−4.29**	*−3.25*	*3.71*
91° p_3	19.04	21.16	23.06	25.03	27.32	30.45	34.98	44.76
p	*72.80*	*44.50*	*24.59*	*11.42*	*3.57*	**0.29**	*1.29*	*9.77*
100° p_3	22.01	24.34	26.29	28.39	30.19	34.20	39.83	50.14
p	*75.77*	*47.68*	*27.82*	*14.78*	*6.44*	**4.04**	*6.14*	*15.15*
116° p_3	27.35	29.91	32.06	34.37	37.08	40.90	47.28	59.30
p	*81.11*	*53.25*	*33.59*	*20.76*	*13.33*	**10.74**	*13.59*	*24.31*
120° p_3	28.83	31.45	33.64	35.88	38.70	42.58	49.22	61.61
p	*82.59*	*54.79*	*35.17*	*22.27*	*14.95*	**12.42**	*15.53*	*26.62*
				Krypton; ρ = 0.345A				
r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20	4.25
V	24.300	25.259	26.243	27.252	28.287	29.348	30.435	31.548	32.688
ν	1.722	1.581	1.440	1.307	1.182	1.064	0.952	0.845	0.742
$-\partial \ln \nu/\partial V$	0.0868	0.0918	0.0955	0.0967	0.0982	0.100	0.104	0.109	0.117
p_1	19.04	5.06	−5.73	−13.93	−20.01	−24.44	−27.50	−29.49	−30.63
p_2	6.63	6.44	6.10	5.60	5.15	4.73	4.40	4.09	3.85
0° p	*25.67*	*11.50*	*0.37*	*−8.33*	*−14.86*	*−19.71*	*−23.10*	*−25.40*	*−26.78*
20° p_3	0.78	0.93	1.12	1.31	1.51	1.74	2.05	2.40	2.85
p	*26.45*	*12.43*	*1.49*	*−7.02*	*−13.35*	*−17.97*	*−21.05*	*−23.00*	*−23.93*
40° p_3	3.75	4.26	4.77	5.17	5.59	6.03	6.63	7.33	8.25
p	*29.42*	*15.76*	*5.14*	*−3.16*	*−9.27*	*−13.68*	*−16.47*	*−18.07*	*−18.53*
60° p_3	7.53	8.34	9.10	9.62	10.18	10.78	11.61	12.63	13.93
p	*33.20*	*19.84*	*9.47*	*1.29*	*−4.68*	*−8.93*	*−11.49*	*−12.77*	*−12.85*
80° p_3	11.56	12.67	13.67	14.25	14.91	15.64	16.69	17.95	19.67
p	*37.23*	*24.17*	*14.04*	*5.92*	*0.05*	*−4.07*	*−6.41*	**−7.45**	*−7.11*
100° p_3	15.73	17.08	18.26	18.96	19.72	20.55	21.83	23.34	25.45
p	*41.40*	*28.58*	*18.63*	*10.63*	*4.86*	*0.84*	*−1.29*	**−2.06**	*−1.33*
108° p_3	17.40	18.87	20.12	20.96	21.64	22.54	23.88	25.51	27.76
p	*43.07*	*30.37*	*20.49*	*12.63*	*6.78*	*2.83*	*0.78*	**0.11**	*0.98*
116° p_3	19.08	20.66	21.99	22.75	23.58	24.51	25.94	27.66	30.05
p	*44.75*	*32.16*	*22.36*	*14.42*	*8.72*	*4.80*	*2.84*	**2.26**	*3.27*
120° p_3	19.93	21.55	22.93	23.71	24.55	25.50	26.97	28.75	31.24
p	*45.60*	*33.05*	*23.30*	*15.38*	*9.69*	*5.79*	*3.87*	**3.38**	*4.46*
140° p_3	24.18	26.05	27.62	28.47	29.40	30.46	32.12	34.20	37.07
p	*49.85*	*37.55*	*27.99*	*20.14*	*14.54*	*10.75*	*9.02*	**8.80**	*10.29*

$\rho = 0.345$A even for neon. One might expect the minimum of the melting point isotherm to lie on the zero pressure axis or slightly below instead of above it. This could be accomplished by assuming a larger value for ρ.

THERMAL EXPANSION

The intercept of an isotherm on the axis of zero pressure gives the position of equilibrium for the temperature of that isotherm. From these intercepts, the thermal expansion coefficient may

easily be determined theoretically. Krypton is the only one of the rare gases for which there are sufficient data to compare theoretical expansion with experiment. The crosses on the graph indicate the experimental interatomic distances. One sees that the calculated expansion is 1.5 to 1.8 times the measured one.

It was thought that the theoretical values for expansion might be brought into agreement with experiment by introducing the effect of dipole-quadrupole interaction. To do this, a term A_2r^{-8} was added to A_1r^{-6} of the van der Waals energy, and it was assumed that A_1 and A_2 are in the same ratio as the dipole-dipole and dipole-quadrupole coefficients calculated theoretically by Buckingham.[14] The values of A_1, A_2, and B are shown in Table III(b). The elastic constants[15] are given in Table VIII and the pressures in Table IX. The minimum of the potential energy curve lies at the same place as that for dipole-dipole interaction alone.

The effect of this modification on the isotherms is shown in Fig. 3. The continuous lines represent the dipole-dipole interaction alone, while the dotted lines include the effect of dipole-quadrupole interaction.[16]

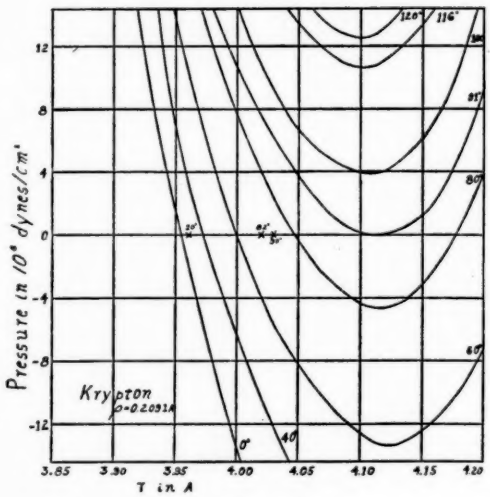

FIG. 2. p–r isotherms for krypton ($\rho = 0.2091$A).

[14] R. A. Buckingham, Proc. Roy. Soc. **A160**, 94, (1937). Cf. H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

[15] The summations for the potential energy of attraction using the inverse sixth and eighth powers are taken from Lennard-Jones, reference 4. The summations involving these powers for the elastic constants are taken from A. May, Phys. Rev. **52**, 339 (1937).

[16] (The B chosen is not the one best suited; therefore the isotherms at low temperature lie a little to the right of the correct lattice distance. A slight change in B should not alter the shape or relative positions of the isotherms. So in order to compare these two sets of curves, the whole second set was simply shifted until the isotherm for zero temperature of the second set passed through the equilibrium position of zero pressure, 3.95A). The curves of the second set almost coincide with those of the first set. At low temperatures, there is no change in expansion, while at higher temperatures the agreement with experimental values is worse. The discrepancy may be due to the fact that the

TABLE VI (*Continued*).

				Xenon; $\rho = 0.2091A$					
r	4.25	4.30	4.35	4.40	4.45	4.50	4.55	4.60	4.65
V	32.69	33.86	35.05	36.27	37.52	38.80	40.11	41.45	42.81
ν	2.426	2.111	1.829	1.575	1.346	1.137	0.946	0.766	0.590
$-\partial \ln \nu/\partial V$	0.125	0.125	0.127	0.129	0.133	0.140	0.152	0.176	0.215
p_1	45.37	13.93	−8.29	−23.62	−33.83	−40.27	−43.96	−45.65	−45.91
p_2	13.43	11.75	10.29	9.04	7.96	7.06	6.36	6.00	5.63
0° p	*58.80*	*25.68*	*2.00*	*−14.58*	*−25.87*	*−33.21*	*−37.60*	*−39.65*	*−40.28*
88° p_3	16.27	17.52	18.88	20.37	22.07	24.20	27.33	33.04	41.80
p	*75.07*	*43.20*	*20.88*	*5.79*	*−3.80*	*−9.01*	**−10.27**	*−6.61*	*1.52*
117° p_3	24.72	26.20	27.72	29.47	31.54	34.18	38.20	45.68	57.37
p	*83.52*	*51.88*	*29.72*	*14.89*	*5.67*	*0.97*	**0.60**	*6.03*	*17.09*
120° p_3	25.19	27.10	28.63	30.42	32.51	35.21	39.32	47.01	58.91
p	*83.99*	*52.78*	*30.63*	*15.84*	*6.64*	*2.00*	**1.72**	*7.36*	*18.63*
160° p_3	37.63	39.27	41.04	43.14	45.67	49.05	54.37	64.56	80.29
p	*96.43*	*64.95*	*43.04*	*28.56*	*19.80*	**15.84**	*16.77*	*24.91*	*40.01*
				Xenon; $\rho = 0.345A$					
r	4.25	4.30	4.35	4.40	4.45	4.50	4.55	4.60	4.65
V	32.69	33.86	35.05	36.27	37.52	38.80	40.11	41.45	42.81
ν	1.656	1.513	1.379	1.253	1.135	1.023	0.918	0.818	0.723
$-\partial \ln \nu/\partial V$	0.0775	0.0775	0.0780	0.0788	0.0801	0.0816	0.0844	0.0886	0.0943
p_1	23.49	7.94	−4.18	−13.48	−20.51	−25.69	−29.38	−31.87	−33.41
p_2	5.69	5.20	4.77	4.38	4.03	3.70	3.44	3.22	3.02
0° p	*29.18*	*13.14*	*0.59*	*−9.10*	*−16.48*	*−21.99*	*−25.94*	*−28.65*	*−30.39*
88° p_3	11.99	12.37	12.81	13.30	13.89	14.47	15.30	16.41	17.82
p	*41.17*	*25.51*	*13.40*	*4.20*	*−2.59*	*−7.52*	*−10.64*	*−12.24*	*−12.57*
140° p_3	21.78	22.19	22.75	23.38	24.13	24.94	26.15	27.82	29.99
p	*50.96*	*35.33*	*23.34*	*14.28*	*7.65*	*2.95*	*0.21*	**−0.83**	*−0.40*
144° p_3	22.54	22.96	23.50	24.15	24.91	25.75	27.00	28.71	30.93
p	*51.72*	*36.10*	*24.09*	*15.05*	*8.43*	*3.76*	*1.06*	**0.06**	*0.54*
160° p_3	25.59	26.03	26.60	27.27	28.09	28.99	30.35	32.23	34.68
p	*54.77*	*39.17*	*27.19*	*18.17*	*11.61*	*7.00*	*4.41*	**3.58**	*4.29*

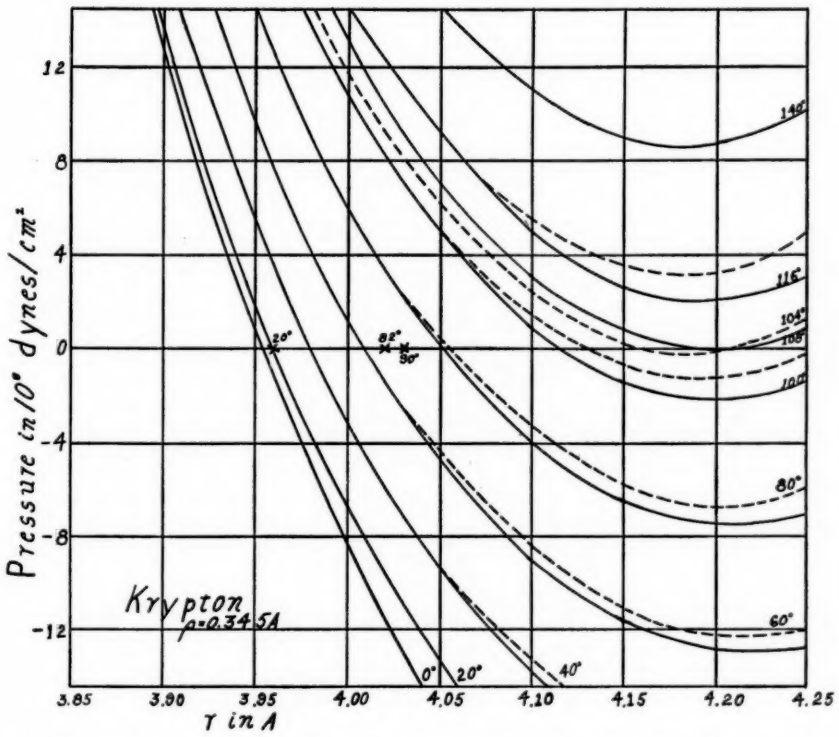

FIG. 3. p–r isotherms for krypton ($\rho=0.345$A). Broken lines include the influence of dipole-quadrupole interaction.

In these calculations, the crystal has been considered as completely ordered. A number of attempts have been made to treat the melting of argon[17] as a disorder phenomenon. The introduction of the influence of disorder into the above calculations would increase the pressure at higher temperatures and therefore further increase the theoretical expansion coefficient.

SPECIFIC HEATS

The data on θ, and U for each volume given in Tables II–IV as well as the expansion coefficient enables one to determine the specific heat curve for constant pressure from the formula

$$C_p=\left(\frac{\partial H}{\partial T}\right)_p=\frac{\partial U_{\text{Total}}}{\partial T}+p\frac{\partial V}{\partial T}. \qquad (10)$$

The second term is so small that it may be neglected. The U total used here is equal to the $-U$ of Eq. (3) plus E, the energy of the heat motion.

$$C_p=(\partial/\partial T)(-U+E)_p. \qquad (10')$$

The values of $(-U+E)$ for the equilibrium positions at zero pressure were plotted against T and differentiated graphically to obtain C_p. Table X gives the results for argon and krypton, and Fig. 4 shows how the theoretical values

TABLE VII. *Debye functions and melting points.*

	ρ IN CM^{-3}	θ (CALC.)	θ (EXP.)	T_b (CALC.)	T_m (EXP.)
Neon	0.2091	60.1	64	14°	24.5
	0.345	52.7	64	21°	24.5
Argon	0.2091	105	80	65°	83.8
	0.250	96.4	80	—	83.8
	0.300	94.4	80	—	83.8
	0.345	80.5	80	76°	83.8
Krypton $-\phi_1=Ar^{-6}$	0.2091	91.1	63	91°	116.0
	0.345	68.3	63	108°	116.0
$-\phi_1=A_1r^{-6}+A_2r^{-8}$	0.345	69.6	63	104°	116.0
Xenon	0.2091	86.7	55	117°	161.3
	0.345	65.4	55	144°	161.3

measurements were made by two different observers. Since the experimental error is quite high (±0.02A) it is not too safe to compare absolute values to obtain expansion coefficients.

[17] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A169**, 317 (1939) and O. K. Rice, J. Chem. Phys. **7**, 136, (1939). Cf. also F. C. Frank, Proc. Roy. Soc. **A170**, 182 (1939).

TABLE VIII. *Krypton $\rho=0.345A$, $\varphi=-(A_1r^{-6}+A_2r^{-8})+A_1Be^{-r/\rho}$. Frequency, elastic constants and energy as in Table IV.*

r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20	4.25
θ	83.74	76.42	69.59	63.17	57.14	51.41	45.99	40.82	35.81
$c_{11}\times10^{-10}$	5.620	4.514	3.598	2.837	2.208	1.686	1.257	0.8342	0.6183
$c_{12}\times10^{-10}$	3.372	2.708	2.158	1.702	1.324	1.012	0.7553	0.5452	0.3739
$c_{44}\times10^{-10}$	3.155	2.638	2.202	1.832	1.519	1.254	1.030	0.8412	0.6825
$-\frac{N\Phi}{2}$	11.715	11.848	11.858	11.768	11.597	11.365	10.982	10.763	10.418
$3/2Nh3/4\nu$	0.783	0.715	0.651	0.591	0.534	0.481	0.430	0.382	0.335
$+U$	10.932	11.133	11.207	11.177	11.063	10.884	10.552	10.381	10.083

TABLE IX. *Krypton $\rho=0.345A$, $\varphi=-(A_1r^{-6}+A_2r^{-8})+A_1Be^{-r/\rho}$. Pressure, volume, and frequency as in Table VI.**

r	3.85	3.90	3.95	4.00	4.05	4.10	4.15	4.20	4.25
V	24.30	25.26	26.24	27.25	28.29	29.35	30.43	31.55	32.69
ν	1.766	1.611	1.467	1.332	1.205	1.084	0.9797	0.8607	0.7551
$-\partial \ln \nu/\partial V$	0.0958	0.0953	0.0955	0.0964	0.0982	0.1010	0.1047	0.1106	0.1195
p_1	21.27	6.85	−4.30	−12.79	−19.12	−23.74	−26.96	−29.07	−30.31
p_2	7.51	6.81	6.21	5.69	5.25	4.86	4.50	4.22	4.00
$0°p$	*28.78*	*13.66*	*1.91*	*−7.10*	*−13.87*	*−18.88*	*−22.46*	*−24.85*	*−26.31*
$20°p_3$	0.80	0.93	1.09	1.27	1.48	1.73	2.02	2.39	2.88
p	*29.58*	*14.59*	*3.00*	*−5.88*	*−12.39*	*−17.15*	*−20.44*	*−22.46*	*−23.43*
$40°p_3$	4.05	4.35	4.70	5.08	5.52	6.03	6.62	7.38	8.39
p	*32.83*	*18.01*	*6.61*	*−2.02*	*−8.35*	*−12.85*	*−15.84*	*−17.47*	*−17.92*
$60°p_3$	8.19	8.56	9.01	9.51	10.10	10.81	11.61	12.71	14.19
p	*36.97*	*22.22*	*10.92*	*2.41*	*−3.77*	*−8.07*	*−10.85*	**−12.14**	*−12.12*
$80°p_3$	12.64	13.05	13.54	14.12	14.82	15.70	16.72	18.13	20.07
p	*41.42*	*26.71*	*15.45*	*7.02*	*0.95*	*−3.18*	*−5.74*	**−6.72**	*−6.24*
$100°p_3$	17.23	17.63	18.15	18.76	19.62	20.62	21.88	23.59	25.97
p	*46.01*	*31.29*	*20.06*	*11.66*	*5.75*	*1.74*	*−0.58*	**−1.26**	*−0.34*
$104°p_3$	18.15	18.55	18.92	19.76	20.59	21.64	22.91	24.67	27.16
p	*46.93*	*32.21*	*20.83*	*12.66*	*6.72*	*2.76*	*0.45*	**−0.18**	*0.85*
$116°p_3$	20.92	21.33	21.88	22.58	23.46	24.64	26.02	27.96	30.70
p	*49.70*	*34.99*	*23.79*	*15.48*	*9.59*	*5.76*	*3.56*	**3.11**	*4.39*
$140°p_3$	26.54	26.93	27.51	28.29	29.30	30.64	32.22	34.55	37.81
p	*55.32*	*40.59*	*29.42*	*21.19*	*15.43*	*11.76*	*9.76*	**9.70**	*11.50*

* Total pressures are in italics; minimum pressures are in boldface type.

compare with the specific heats measured by Clusius.[10] Again the values obtained by using $\rho=0.345$A are in better agreement with experiment than those obtained by using $\rho=0.2091$A. A slightly higher value of ρ would improve matters greatly. The introduction of the dipole-quadrupole interaction changes the theoretical specific heats only slightly at higher temperatures. For this reason, the specific heat curve furnishes probably the surest means of determining the value of ρ.

COMPRESSIBILITIES

As Brillouin[18] has pointed out, the elastic constants c_{11}, c_{12}, and c_{44} are not the ones measured by macroscopic experiments, since a contribution from the heat motion must be included. In fact our compressibilities are not $3/(c_{11}+2c_{12})$ but depend on p_3.

No experiments have been made on the com-

TABLE X. *Specific heats at constant pressure.*

T	EXPERIMENTAL	THEORETICAL ($\rho=0.2091$A)	THEORETICAL ($\rho=0.345$A)
	Argon		
20°	2.82	2.05	3.15
30°	4.40	4.33	4.70
40°	5.30	5.35	5.83
50°	5.90	6.54	6.74
60°	6.41	12.47	8.06
70°	6.97		11.14
	Krypton		
20°	3.65		3.76
40°	5.66	4.98	5.82
60°	6.29	7.45	6.80
80°	6.81	11.13	8.88
100°	7.49		9.20

[18] L. Brillouin, Ann. d. physique (10) **4**, 528 (1925); Comptes rendus **192**, 668 (1931).

pressibilities of the rare gases in the solid form. The following theoretical formula for compressibility has been used by Clusius:

$$\chi = 1.75 \times 10^{-6}(A^{\frac{1}{3}}d^{\frac{1}{3}}\theta).$$

A is the atomic weight, d the density and θ the Debye characteristic temperature. His values are compared in Table XI with K, those obtained from the slope of the p-r curve at 0°. The formula used by Clusius does not take into account the cross-tensions in the forces acting on an oscillating particle.[19]

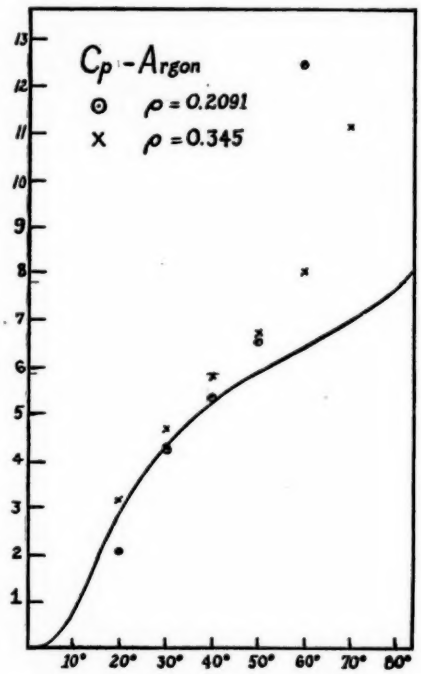

FIG. 4. Specific heat curve for argon. Theoretical values shown by circles and crosses.

TABLE XI. *Compressibilities in* $(10^{12}$ *dynes/cm*$^2)^{-1}$.

	NEON	ARGON	KRYPTON	XENON
		$\rho = 0.2091A$		
$\frac{3}{c_{11}+2c_{12}}$	214	35.2	22.6	18.5
K*	143	33.6	21.9	17.7
χ	53	20	16	15
		$\rho = 0.345A$		
$\frac{3}{c_{11}+2c_{12}}$	245	57.8	39.8	32.2
K*	206	52.5	39.2	30.8
χ	53	20	16	15

* K includes the influence of zero point pressure.

Further experimental data such as compressibilities and thermal expansion would enable one to test better the validity of results. The values of A and B obtained in this paper may be applied to the calculation of the second and third virial coefficients. At present, experimental data for the virial coefficients are available only for neon and argon.[20]

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Professor K. F. Herzfeld for suggesting the present problem, and for his constant assistance during its solution; to Doctor Albert May for a number of suggestions, and to Professor K. Clusius for the use of some data prior to their publication.

[19] A. Eucken, *Handbuch der Experimental Physik*, Vol. 8, No. 1 (1929), p. 249.

[20] H. Kammerlingh Onnes and C. A. Crommelin, Leiden Communication **118B**, 24 (1910). L. Holborn and J. Otto, Zeits. f. Physik **33**, 1 (1925). J. R. Roebuck and H. Osterburg, Phys. Rev. **46**, 785 (1934).

The Rotational Partition Function of the Water Molecule*

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The rotational contribution to the partition function of the water molecule has been computed for temperatures up to 298.1°K by summing the experimental energy levels of Randall, Dennison, Ginsberg and Weber. The results are compared with those of a rigid rotator and in this way the "stretching" contribution is determined. E. Bright Wilson's theoretically deduced stretching correction compares very favorably with the values obtained by summing energy states.

THE computation of the thermodynamic functions of the water molecule from spectroscopic data has been the subject of several papers. These computations have been based on Mecke's interpretation of the seventeen known vibration-rotation bands of the water molecule.[1] Mecke's analysis extended to only a few rotational levels with J greater than four or five. For this reason the effect of centrifugal distortion could not be determined, and the moments of inertia given are average values over the lower rotational states. With only these data available, A. R. Gordon[2] was forced to treat the molecule as a rigid rotator in order to obtain the approximate rotational partition function.

For many light molecules the contribution of centrifugal distortion to the partition function is appreciable at ordinary temperatures. Using classical mechanics, E. Bright Wilson[3] obtained an expression for this distortional contribution in terms of the force constants of the molecule. According to this author, the partition function for the rigid rotator must be multiplied by a correction term $(1+\rho T)$, where ρ is a constant to a first order of approximation. Wilson gives ρ the value 2.04×10^{-5} for the water molecule. This correction increases the specific heat of steam by $2\rho RT$, which amounts to almost one-half percent of C_{rot} at room temperature.

Randall, Dennison, Ginsburg and Weber[4] have recently published an analysis of the infrared spectrum of water which extends to sufficiently high energy levels to make possible the exact computation of the rotational partition function up to room temperature by directly summing the experimentally observed energy levels. Because of the importance of the water molecule, it seemed advisable to carry out this rather laborious computation and thus to check the "stretching" correction given by Wilson.

The rotational energy levels of an asymmetric top are characterized by a total angular momentum quantum number J and a pseudo quantum number τ. For a given value of J there are $(2J+1)$ sub-levels for which τ takes the values $-J, -J+1, \cdots J-1, J$. The levels with even values of τ, $(0, \pm2, \cdots)$ have the weight factor $(2J+1)i(2i+1)$ and are known as para states. The ortho states have odd values of τ, $(\pm1, \pm3, \cdots)$, and have a weight factor $(2J+1)(i+1)(2i+1)$, where i, the nuclear spin of the hydrogen atom, is $\frac{1}{2}$. The exact rotational partition function for the ground vibrational state is then obtained by direct summation.

$$Q_{\text{rot}}(\text{para}) = \sum_{J=0}^{\infty} \sum_{\tau} (2J+1) e^{-E(J,\tau)/kT}$$

$$-J \leqq \tau \text{ (even values only)} \leqq J.$$

$$Q_{\text{rot}}(\text{ortho}) = 3\sum_{J=0}^{\infty} \sum_{\tau} (2J+1) e^{-E(J,\tau)/kT}$$

$$-J \leqq \tau \text{ (odd values only)} \leqq J,$$

and Q_{rot} (equilibrium) $= Q_{\text{rot}}$ (para) $+ Q_{\text{rot}}$ (ortho), where $E(J, \tau)$ are the energy levels given by Randall, Dennison, Ginsburg and Weber, with their proper designations in terms of J and τ.

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 421.

[1] Mecke, Zeits. f. Physik **81**, 313 (1933); Baumann and Mecke, *Ibid.* **81**, 445 (1933); Freudenberg and Mecke, *Ibid.* **81**, 465 (1933).

[2] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).

[3] E. Bright Wilson, J. Chem. Phys. **4**, 526 (1936).

[4] Randall, Dennison, Ginsburg and Weber, Phys. Rev. **52**, 160 (1937).

For the highest temperature at which the summation was performed (300°K), the experimental data did not extend to sufficiently high J values and it was necessary to use an extrapolation method similar to that described by Gordon and Barnes[5] in order to estimate the levels above $J=11$. The total contribution of the extrapolated levels to Q, Q' and Q'', is only 0.1 percent, 0.4 percent and 1.5 percent, respectively, and the maximum error introduced into C_{rot} at 300°K cannot well be greater than 0.05 percent.

Due to the noncombining nature of the ortho and para states and also to the small moments of inertia of the water molecule, the specific heat of steam at low temperature will have the same interesting features shown by hydrogen. Table I contains C_{rot}/R for ortho, para, "normal," and "equilibrium" steam, and Fig. 1 shows these quantities plotted against absolute temperature. Normal water, like hydrogen, consists of 25 percent para and 75 percent ortho modifications.

At 100°K, C_{rot} of the ortho, para and equilibrium forms are nearly identical. At temperatures above 100°K, the rise of C_{rot}/R above the classical value of $\frac{3}{2}$ is due to the contribution of centrifugal distortion since C_{rot}/R for a rigid asymmetrical rotator approaches $\frac{3}{2}$ at high temperatures. From Table I it is evident that the stretching contribution to C_{rot}/R amounts to 0.0047 at 100°K, 0.0070 at 150°K, 0.0093 at 200°K and 0.0140 at 300°K. These three quantities are used to evaluate ρ in Wilson's correction term $2\rho T$, and lead to values 2.35×10^{-5}, 2.33×10^{-5}, 2.32×10^{-5} and 2.33×10^{-5}, respectively. The average of these four values is 2.33×10^{-5}. Wilson's theoretical evaluation of ρ, (2.04×10^{-5}), is in good agreement with these results, but is not as reliable.

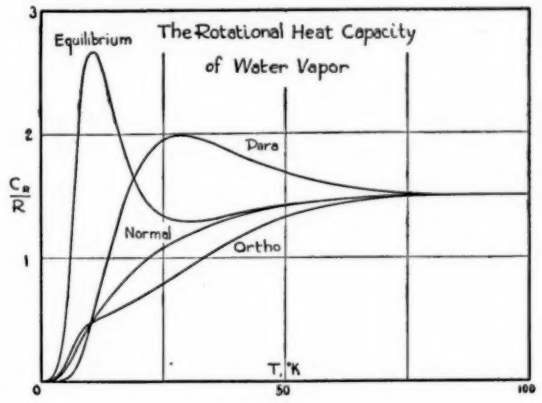

FIG. 1.

TABLE I. C_{rot}/R.

T, °K	PARA (EVEN)	ORTHO (ODD)	EQUILIBRIUM MIXTURE	NORMAL MIXTURE	PERCENTAGE PARA IN EQUILIBRIUM MIXTURE
5	0.0083	0.1384	0.4656	0.1059	99.01
10	0.4287	0.4653	2.6753	0.4562	76.05
15	1.1930	0.5722	2.1366	0.7274	49.97
20	1.7273	0.6687	1.5593	0.9334	37.02
25	1.9538	0.7856	1.3385	1.0776	31.04
30	1.9825	0.9168	1.2889	1.1832	28.15
40	1.8320	1.1627	1.3462	1.3300	25.90
50	1.6781	1.3319	1.4207	1.4184	25.27
70	1.5395	1.4709	1.4880	1.4880	25.03
100	1.5079	1.5036	1.5047	1.5047	25.01
*150	—	—	1.5070	—	—
200	1.5093	1.5093	1.5093	1.5093	25.00
300	1.5140	1.5140	1.5140	1.5140	25.00

*C_v at 150°K was computed by Professor H. L. Johnston from the same source of data and was kindly furnished to the authors in a private communication.

These computations were carried out in compliance with a suggestion offered by Professor F. G. Keyes, who was particularly interested in obtaining the most accurate specific heat information which spectroscopic data could offer. It is now certain that the most reliable values of $C_p°$ are afforded by adding the stretching correction $(2.33\times10^{-5}\times2RT)$ to the spectroscopic specific heats of Gordon and Barnes for temperatures up to 300°K, and in all probability this method is exceedingly accurate up to 1000°K. The most refined calorimetric data[6] in the neighborhood of room temperature are in good agreement with specific heats calculated in this manner, within the error of the experiment.

[5] A. R. Gordon and C. Barnes, J. Phys. Chem. **36**, 1143 (1932).

[6] S. C. Collins and F. G. Keyes, Proc. Am. Acad. Arts Sci. **72**, 283 (1938).

Some Quantum-Mechanical Considerations in the Theory of Reactions Involving an Activation Energy

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The activated complex or transition state method for calculating the absolute rate of a chemical reaction with an activation energy would be rigorously valid if classical mechanics applied to all degrees of freedom. In quantum mechanics, two kinds of limitations must be considered. First, because of Heisenberg's uncertainty principle, the transition state itself can be defined only if the potential surface is sufficiently flat around the highest point of the reaction path. Second, even if this condition is fulfilled, the transmission coefficient can differ from the value expected on the basis of classical mechanics, because a wave packet can be reflected both on its way up, and also on its way down the potential barrier separating the initial and final states. In fact, the transmission coefficient is, in many cases, a rapidly fluctuating function of the energy of the system. If the temperature distribution of the energy is sufficiently broad to cover several periods of this fluctuation, an average transmission coefficient can be defined which nearly agrees with the classical value. For the crossing of a one-dimensional potential barrier, the quantum corrections are surprisingly small. In problems with several degrees of freedom, the transmission coefficient is affected by the interchange of translational and vibrational energy. However, if the vibrational motion is fast as compared with the motion along the reaction path, these degrees of freedom can be treated on a par with the electronic coordinates. In this case, the formulas of Eyring, with a mechanically sensible transmission coefficient, are satisfactory. On the whole, we conclude that quantum-mechanical considerations invalidate the transition state method to a much smaller extent than could be presumed and it is only in the consideration of the relative rates of reactions between isotopes and reactions at very low temperatures that these effects may be important.

I. The Transition State Method and Its Validity

It is well known that whenever classical mechanics is valid, the formula[1]

$$k=(P_t/P_i)(\delta/\bar{v})^{-1}\gamma=P_t\bar{v}\gamma/(P_i\delta) \qquad (1)$$

for the rate, k, of reactions with an activation energy is a direct consequence of statistical mechanics. In (1), P_t is the probability of the transition state in thermal equilibrium. The transition state is a strip of width δ in configuration space. This strip lies across the deepest saddle on the energy mountain separating the two regions in configuration space which correspond, respectively, to the initial and final state of the reaction. P_i is the probability of the system being in the initial state; $\bar{v}$ is the average velocity with which the configuration points cross the saddle; $\delta/\bar{v}$ their average time of sojourn in the transition state. Finally, γ expresses the probability that a system which crosses the saddle at complete thermal equilibrium actually originated in the initial state and will proceed to the final state to complete the chemical reaction.[2] The transmission coefficient, γ, is the only quantity appearing in Eq. (1) which cannot be evaluated by well-known methods of statistical mechanics —it can be estimated only from the general shape of the potential mountain.

There is no reaction with an activation energy in which classical mechanics is valid for all parts of the reacting system. However, it appears logical[3] to replace the classical expressions for P_t and P_i in (1) by the corresponding quantum theoretical sums. The question as to what extent this is justifiable has been discussed repeatedly.[4] One difficulty is that the notion of an activated

* Now at Princeton University.

[1] This equation was first proposed by A. Marcelin, Ann. chim. phys. (9)3, 120, 185 (1915). Subsequent treatments of this nature have been given by A. March, Physik. Zeits. **18**, 53 (1917); Pelzer and Wigner, Zeits. f. physik. Chemie **B15**, 445 (1932); E. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932); H. Eyring, J. Chem. Phys. **3**, 107 (1935); Evans and Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

[2] A more detailed explanation of (1) will be found, e.g. Trans. Faraday Soc. **34**, 29 (1938). The reaction is considered "completed" when the distance between the reaction products becomes large compared with molecular dimensions. This has a clear sense only in gas reactions where the products separate at once to very large distances (of the order of the mean free path) if they begin to separate at all.

[3] This was first done by E. Wigner (Zeits. f. physik. Chemie **B19**, 203 (1932). It was also the method adopted by H. Eyring in developing his formulae of great generality.

[4] See for example, E. Wigner, Trans. Faraday Soc. **34** 29 (1938).

or transition state is not strictly compatible with the laws of quantum mechanics. The transition state method can only be justified when the path of the reaction is sufficiently flat in the neighborhood of the transition state so that we can consider simultaneously the position and the velocity of the point representing the system in configuration space. In classical mechanics, δ is always considered to be so small that the potential is practically constant across the transition state. If δ is large, P_t and the average length of time that the system spends in the transition state become rather complicated functions of δ and (1) no longer applies. In quantum mechanics, it is necessary to take the width of the transition state sufficiently great to allow reducing the uncertainty in the velocity, Δv, to a small fraction of the average thermal velocity, $\bar{v}$. Certainly, if we are to apply Maxwell's formula, $\exp(-mv^2/2kT)$, for the probability of a system with a mass m to have the velocity v at the temperature T, the spread in the velocity, Δv, due to the uncertainty principle must be so small that it makes little difference whether we use the upper bound, $v+\Delta v/2$, or the lower bound, $v-\Delta v/2$, in the exponential. This means that $mv\Delta v$ must be small compared with kT. Putting $(kT/m)^{\frac{1}{2}}$ for v, this gives $\Delta v \ll (kT/m)^{\frac{1}{2}}$. We must take the transition state sufficiently wide so that this last relation can be satisfied. On the other hand, this width must be sufficiently small so that it is still a good approximation to take P_t proportional to δ. Thus, if the energy surface in the vicinity of the saddle has a curvature in the direction of the reaction path corresponding to the parabola, $V=V_0-aX^2$, we must confine the activated state to a strip across the path which is so thin that $\exp(-aX^2/kT)$ shall be nearly unity all over the strip. This means that $\delta \ll (kT/a)^{\frac{1}{2}}$. These limits for the maximum values of Δv and of δ are only compatible with the quantum-mechanical uncertainty principle if:

$$\frac{h}{2\pi} < \delta m \Delta v \ll m(kT/a)^{\frac{1}{2}}(kT/m)^{\frac{1}{2}}.$$

Thus the transition state can only be defined when the curvature of the energy surface satisfies the condition:

$$(h/2\pi)(a/m)^{\frac{1}{2}} \ll kT. \qquad (2)$$

Apart from an unimportant numerical factor, the left side of this equation is the zero point energy of a mass, m, in a potential, $+aX^2$. Thus, Eq. (1) and the transition states method can be justified only if this virtual zero point energy is smaller than kT. If Eq. (2) is satisfied and if the dependence of the potential on the coordinates along the strip does not change appreciably from one side of the strip to the other, the transition state can be defined sufficiently accurately for deriving Eq. (1) in spite of the limitations of quantum mechanics. Fortunately, this is fulfilled in many important cases.

The computation of γ presents another difficulty in the quantum-mechanical applications. As long as the reacting system behaves classically, γ can be estimated from simple geometrical and mechanical arguments. Usually the coordinates in configuration space are chosen so that the kinetic energy is the product of an effective mass and the sum of squares of the generalized velocities. In such coordinate systems, molecular collisions are kinematically equivalent to the rolling of a ball on a surface whose height is proportional to the potential energy of the corresponding molecular configuration. The question whether a given collision will result in a chemical reaction can be answered by examining the trajectory of the ball when it is shot in the corresponding manner. However, when quantum theory is used, the ball must be replaced by a wave packet. In some reactions γ will retain its classical value. In others, due primarily to the diffraction of the wave packets, it will have a different magnitude. Thus γ can be much smaller than unity in quantum-mechanical systems even for an energy surface for which a mechanical picture does not indicate an appreciable probability of reflection. Consequently, the use of Eq. (1) with seemingly reasonable values of γ can lead to erroneous rates even when the condition of (2) is fulfilled.

If the condition (2) is not fulfilled, (1) must certainly be corrected to take into account the quantum-mechanical penetration of the potential barrier.[5] But it may not be possible to use a

[5] R. E. Langer; Born and Franck, C. Eckart, Phys. Rev. **35**, 1303 (1930); R. P. Bell, Proc. Roy. Soc. **A139**, 466 (1933). That (2) is the condition for the absence of an appreciable amount of tunneling is evident also from the

penetration factor in any simple way to correct for the deviations from classical theory. If Eq. (2) is not fulfilled, a reflection after the crossing of the saddle (which is usually taken into account by choosing an appropriate value of γ) cannot be distinguished from a failure to cross the saddle. Thus it would no longer be possible to define a transmission coefficient.

II. The Transmission Coefficient

A. We shall first carry out a rather formal consideration concerning transmission coefficients, which will be based on the assumption that there is a definite probability for a system, which has crossed the transition state, to be reflected back to the transition state. This probability will be denoted by ρ_i and ρ_f for crossings from left to right and right to left, respectively. It will be assumed that these probabilities are equal for systems originating from the two sides of the transition state and are independent of the number of times the system has already crossed the transition state.

The value of the transmission coefficient, γ, depends of course on the exact nature of the reaction surface. It is unity if all systems cross the transition state only once in their passage from the initial to the final state or from the final to the initial state. In the general case, some of the systems[6] which cross the transition state will cross it again in the other direction. This may happen repeatedly before the atoms of the system finally separate, either to form the same molecules which originally collided, or else to form the molecules corresponding to the completed reaction. Thus some trajectories which cross the transition state from left to right will not lead to a chemical reaction and others may require many crossings before the reaction is completed.

At complete thermal equilibrium, half of the systems in the transition state are moving from left to right and the other half from right to left.

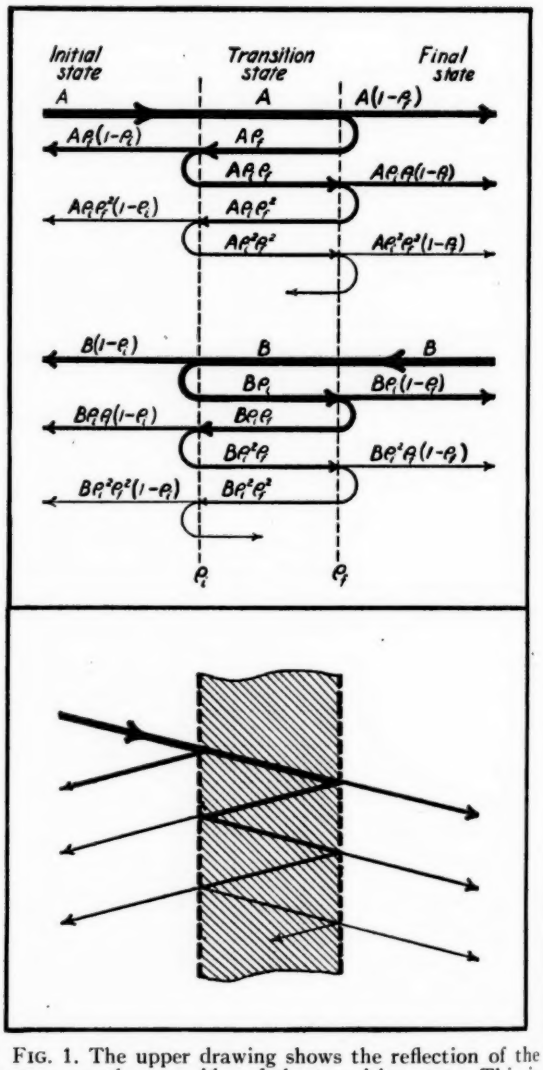

FIG. 1. The upper drawing shows the reflection of the systems on the two sides of the transition state. This is similar to the reflection of a beam of light at the air-glass and glass-air interfaces in passing through the plate glass shown in the lower figure.

The transmission coefficient, γ, is the fraction of the systems moving from left to right at complete thermal equilibrium which originally came from the initial state and which will proceed to the final state without first returning to the transition state. At complete thermal equilibrium, A systems arrive, in unit time, at the transition state directly from the initial state and B systems come from the final state. Fig. 1 shows schematically the flux of the different types of systems through the transition region. By simple addition, we see that the total number of systems

formula for the first quantum correction to (1). (Cf. reference 3.)

[6] The term "system" is used here also for the point in configuration space which corresponds to the position of the atoms forming the system. The left side of the transition state is supposed to correspond to the atoms forming the molecules of the reacting substances, the right side corresponds to the reaction product.

crossing the transition state from left to right in unit time is

$$N_{l\to r}=A(1+\rho_i\rho_f+\rho_i^2\rho_f^2+\cdots)+B\rho_i(1+\rho_i\rho_f+\rho_i^2\rho_f^2+\cdots)=(A+B\rho_i)(1-\rho_i\rho_f)^{-1} \quad (3)$$

and the number of those crossing it from right to left is

$$N_{r\to l}=A\rho_f(1+\rho_i\rho_f+\rho_i^2\rho_f^2+\cdots)+B(1+\rho_i\rho_f+\rho_i^2\rho_f^2+\cdots)=(A\rho_f+B)(1-\rho_i\rho_f)^{-1}. \quad (4)$$

At equilibrium $N_{l\to r}=N_{r\to l}$, and hence

$$B=A(1-\rho_f)/(1-\rho_i). \quad (5)$$

Substituting this expression for B into Eq. (3),

$$N_{l\to r}=A/(1-\rho_i). \quad (6)$$

However, the number of systems which have originated in the initial state and which proceed to the final state is seen to be

$$N_{i\to f}=A(1-\rho_f)(1+\rho_i\rho_f+\rho_i^2\rho_f^2+\cdots)=A(1-\rho_f)/(1-\rho_i\rho_f). \quad (7)$$

The transmission coefficient is the ratio of $N_{i\to f}$ to $N_{l\to r}$

$$\gamma=N_{i\to f}/N_{l\to r}=(1-\rho_i)(1-\rho_f)/(1-\rho_i\rho_f). \quad (8)$$

The assumption made at the beginning of this section that the systems crossing the transition state from left to right have the same probability for being reflected no matter whether they originated in the initial or in the final state (or how many times they have already crossed the transition state), is not always justified. We shall see in Section 3 that for a one-dimensional barrier, the transmission coefficient for any one value of the energy does not necessarily satisfy Eq. (8). However, the average transmission coefficient for many systems with slightly different energies will agree with the above expression.

We can compare the transmission of a wave packet through a potential barrier, as considered in this section, with the passage of a beam of light through a piece of plate glass partially silvered on both sides. (See lower part of Fig. 1.) Light of one particular frequency shows a very complicated diffraction pattern. If the direction of the beam is sharply defined, the amount of light passing through the glass depends on the exact wave-length. For light of a range of frequencies, the transmission no longer depends critically on the wave-length and will be given by (8) (provided that the thickness of the plate is large compared with the wave-length). From this analogy we see that Eq. (8) can apply for the average transmission coefficient of an assembly of states in thermal distribution, not, however, for the transmission coefficient of a single quantum state. The example in Section 3 should make this more clear.

B. In classical theory, for low temperatures, ρ_i and ρ_f approach zero as it is very improbable that a system with barely enough energy to cross the activated state will find its way back.[4] For higher temperatures, the reflection coefficients may increase. This must be expected, in particular, if the vibrations in the transition state are less stiff than in the initial state, i.e., for the exceptionally fast reactions.

We shall consider an energy surface on which the energy and vibrational frequency change within a very short distance along the reaction path. The abruptness of the energy change tends to make γ small; while the straightness of the reaction path tends to make it large. We shall suppose that the energy surface at the initial state has a smaller curvature perpendicular to the reaction path than at the final state, but that the minimum energy of the initial state is higher than that of the final state. Fig. 2 shows such an energy surface. All the systems of low energy pass from the initial to the final state, but part of the systems of high energy are reflected. If the potential energy is $V_i=A+a_ix^2$ for the initial and $V_f=a_fx^2$ for the final state, only those systems can be reflected which lie outside the point of intersection, $x'=A^{\frac{1}{2}}/(a_f-a_i)^{\frac{1}{2}}$. This is a negligibly small fraction of the systems at low temperatures and hence $\gamma=1$. The reflection plays an important role only at temperatures so high that $kT>a_ix'^2$. This is equivalent to the condition:

$$A/kT<a_f/a_i-1=(\nu_f/\nu_i)^2-1, \quad (9)$$

where ν_i and ν_f are the vibrational frequencies in initial and final states.

The existence of a limiting temperature, above which γ becomes small, will always be true

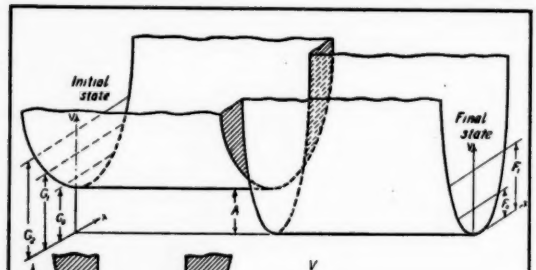

FIG. 2. Potential energy surface illustrating the variation of the transmission coefficient with temperature. From classical mechanical considerations, only those systems can be reflected which have sufficient energy to reach the baffle. The coordinate axes refer to the upper figure.

whenever the frequencies in the transition state are lower than in the initial state. The change in energy between the initial and the final state does not have to take place abruptly nor does the reaction path have to be straight. This becomes evident if we compare the rate of the reverse reaction, according to Eq. (1), with the total number of collisions in which the energy of the colliding particles is greater than A. Clearly, this latter quantity gives an upper limit for the rate.[7] The number of collisions involving energies greater than A is

$$(kT/2\pi m)^{\frac{1}{2}}(A/kT+1)\exp(-A/kT). \quad (10)$$

This must be larger than the reaction rate according to Eq. (1):

$$k=\gamma(\nu_f/\nu_i)(kT/2\pi m)^{\frac{1}{2}}\exp(-A/kT). \quad (11)$$

Thus γ must be less than unity if

$$A/kT<\nu_f/\nu_i-1. \quad (12)$$

The limiting temperature for a transmission coefficient of unity as given by Eq. (12) is about right if the reaction path is straight and the transverse vibration frequencies change slowly along the reaction path. The temperature given by (12) is much higher than that of Eq. (9). This corresponds to the fact that γ is larger for energy surfaces having smooth rather than abrupt changes. In actual chemical reactions, γ will depart from unity somewhere between these two temperatures. *Thus, in general, the transmission coefficient falls below 1 at high temperatures for classical mechanical reasons.* We shall see in the next section that at low temperatures, where γ should be 1 according to classical mechanics, it is also smaller than 1 for quantum-mechanical reasons.

III. One-Dimensional Rate Problems

The simplest examples of reaction rate involve motion in only one dimension. If the activated state method applies, we can divide the calculation of γ into the two easier problems of determining the reflection coefficients ρ_f and ρ_i which refer to the passage from the activated state to the final and to the initial states, respectively. For one-dimensional problems these reflection coefficients are, of course, zero in classical mechanics.

In the special case of Eckart's potential functions,

$$V(X)=A(1+\exp(2\pi X/l))^{-1}, \quad (13)$$

decreases from A to 0, as X increases from large negative values (initial state) to large positive values (final state). The energy drop takes place around $X=0$ in a distance roughly equal to $l/2$ (Fig. 3). The reflection coefficient corresponding to the motion from negative to positive X is:

$$\rho=\left[\frac{\exp(2\pi l(p-q)/h)-1}{\exp(2\pi l(p+q)/h)-1}\right]^2\exp(4\pi lq/h), \quad (14)$$

where $q=(2m(E-A))^{\frac{1}{2}}$ and $p=(2mE)^{\frac{1}{2}}$ are the momenta of the system before and after the potential drop. As this drop becomes abrupt ($l\to 0$), the reflection coefficient becomes

$$\rho=(p-q)^2/(p+q)^2. \quad (15)$$

The explanation of this reflection is similar to that for the reflection of light at a glass to air interface. In quantum mechanics the dynamical system is represented by a wave packet with a wave-length which decreases from h/q to h/p as it passes across the potential drop. The energy change can therefore be expressed as a change in

[7] K. F. Herzfeld, Zeits. f. Physik **8**, 132 (1922); M. Polanyi, Zeits. f. Physik **1**, 337 (1920).

the index of refraction and the analogy with light is complete.

In Fig. 4 we have plotted the reflection coefficient for an H atom when passing across abrupt, steep and gradual Eckart potential drops of 10 kcal. The gradual drop, $l=1.0$A, is still somewhat steeper than those which occur in the majority of chemical reactions. We see that the reflection coefficient approaches zero rapidly as the energy of the system is increased. One will expect, therefore, that the quantum corrections in one-dimensional problems are important only for reactions at very low temperatures involving light molecules or for isotope separations where slight differences in rates are significant.

Strictly speaking, this conclusion holds only if the barrier is so wide that (2) is satisfied, and consequently the method of Section 2 can be used to express the transmission coefficient in terms of the reflection coefficients. Otherwise the transmission must be computed by quantum-mechanical methods. For the sake of concreteness, let us consider a potential barrier with abrupt energy changes (Fig. 5). We denote by p_i, q and p_f the momenta of the system in the initial, transition, and final states. Substituting the reflection coefficient (15) into (8), we would obtain for the transmission coefficient of the barrier:

$$\bar{\gamma}=4qp_ip_f/(q^2+p_ip_f)(p_i+p_f). \qquad (16)$$

In this expression there is no dependence of the transmission coefficient on the width of the barrier, d.

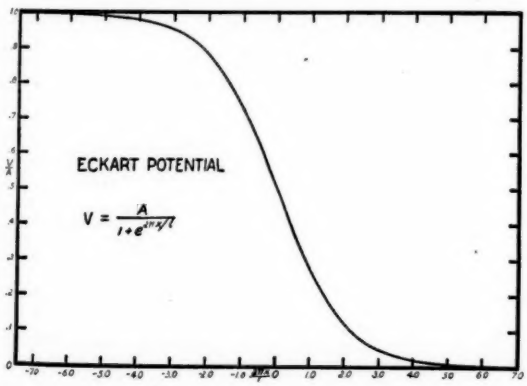

FIG. 3. A special case of the Eckart potential gives a function which changes smoothly from one constant value to another.

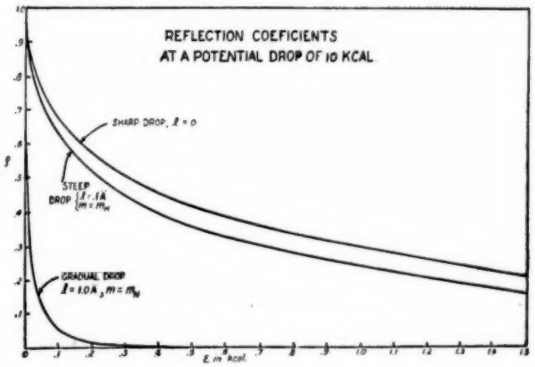

FIG. 4. Probability of reflection at abrupt, steep and gradual potential energy drops as a function of the energy of the system.

One can compute the exact value of the transmission coefficient by fitting together the wave function and its derivative at the discontinuities of the potential energy. One obtains in this way

$$\gamma=\frac{4q^2p_ip_f}{q^2(p_i+p_f)^2\cos^2\varphi+(q^2+p_ip_f)^2\sin^2\varphi}, \qquad (17)$$

where $\varphi=2\pi qd/h$. This is evidently different from (16). If the width of the barrier is not large compared with the wave-length, quantum mechanics prevents us from even defining a transition state. If the barrier is wide enough to justify the activated state method, the exact transmission coefficient of Eq. (17) shows rapid fluctuations with the energy. Averaging γ over a small energy range (which corresponds under these conditions to averaging over φ) one obtains an averaged transmission coefficient, which turns out to be equal to the transmission coefficient of Eq. (16):

$$\bar{\gamma}=\frac{1}{2\pi}\int_0^{2\pi}\gamma d\varphi. \qquad (18)$$

It is only in this sense that Eq. (8) is valid. For any particular energy, the waves reflected at the two discontinuities of the potential interfere with each other to aid or to hinder the transmission. The effect of this interference averages out, however, for reasonably large energy ranges.

Figure 6 shows γ and $\bar{\gamma}$ plotted as functions of the energy of the impinging particles. Here $A_1=A_2=A=10$ kcal. and $d=1.0$A. The exact

FIG. 5. One-dimensional energy barrier with abrupt changes in the potential.

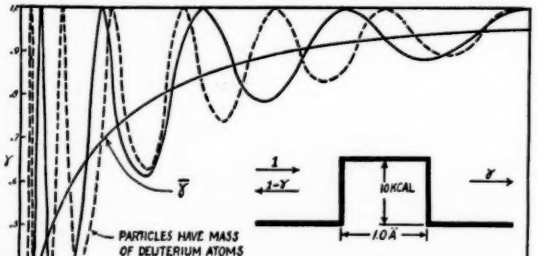
$\bar{\gamma}$
PARTICLES HAVE MASS OF DEUTERIUM ATOMS
PARTICLES HAVE MASS OF HYDROGEN ATOMS
1
1-γ
γ
10 KCAL
1.0 Å
PROBABILITY OF TRANSMISSION OVER ONE DIMENSIONAL POTENTIAL BARRIER
ENERGY OF PARTCLES HITTING BARRIER
10 11 12 13 14 15 16 Kcal 17 18 19 20 21

FIG. 6. Transmission coefficients for H and for D atoms passing over a one-dimensional potential energy barrier.

transmission coefficient, γ, oscillates about $\bar{\gamma}$. The oscillation of the transmission coefficient becomes quicker with increasing mass of the particles. It is interesting to note that the maximum in the transmission coefficient occurs for deuterium before it occurs for hydrogen so that at an energy of 10.2 kcal., the transmission coefficient for the former is about five times greater than for the latter. The situation is reversed, however, at 10.5 kcal.

It seems tempting, at first, to try to utilize the large ratios of transmission coefficients, as shown in Fig. 6, for the separation of isotopes. This is difficult, however, for several reasons. First, because the energy of the reacting systems is not restricted to one single value in actual experiments but covers—according to the Maxwell-Boltzmann distribution formula—a region of appreciable width so that the fluctuations shown in Fig. 6 average out to a large extent. Furthermore, the ratio of transmission coefficients fluctuates not only as a function of the energy but in many dimensional problems also as a function of the other parameters of the problem. As these parameters also cover a range of values for the reacting systems, the fluctuations tend to average out to an even larger extent. Finally, the fluctuations are as pronounced as in Fig. 6 only if the top of the barrier has a flat portion, which is not very much shorter than the wavelength.

On the other hand, one can, in principle, always obtain large separations at very low temperatures, where "tunneling" becomes important. In quantum mechanics, systems with less energy than the activation energy may still react although only with a small probability.[8] The transmission coefficient is still given by (17) where now q is imaginary.

In unit time the number of molecules with an energy between E and $E+dE$ which hit the barrier is proportional to $\exp(-E/kT)dE$. The ratio of the actual rate, k, to the classical rate, k_{class}, is then:

$$\frac{k}{k_{\text{class}}}=\frac{\int_0^A \gamma(E)\exp(-E/kT)dE+\int_A^\infty \gamma(E)\exp(-E/kT)dE}{\int_A^\infty \exp(-E/kT)dE} \tag{19}$$

$$=\frac{k_{\text{through}}}{k_{\text{class}}}+\frac{k_{\text{over}}}{k_{\text{class}}}.$$

[8] Similar calculations were made before particularly by R. P. Bell, J. Chem. Phys. **2**, 164 (1934); Proc. Roy. Soc. **A139**, 466 (1933); H. Eyring and A. Sherman, J. Chem. Phys. **1**, 345 (1933); C. E. H. Banri and G. Ogden, Trans. Faraday Soc. **30**, 432 (1934).

Figure 7 shows the relative number of D atoms which react at 126°K as a function of their energy. There are two peaks in this curve. One corresponds to the reactions, k_{through}, due to penetration of the barrier and the other, k_{over}, corresponds to passage over the barrier. At a slightly higher temperature the penetration is unimportant; at a slightly lower temperature the passage over the barrier is unimportant. At high temperatures, where classical theory is valid, the rate of the crossing of the barrier is $2^{\frac{1}{2}}$ times higher for hydrogen than for deuterium, owing to the higher velocity of the former. Table I shows the rates of crossing, for H and for D, relative to the classical rate of H at 252°. Here k_{trans} is the reaction rate which would be predicted on the basis of the transition state method using the quantum-mechanical value for the reflection coefficients, and Eq. (8)

$$\frac{k_{\text{trans}}}{k_{\text{class}}}=\frac{\int_A^\infty \bar{\gamma}(E)\exp(-E/kT)dE}{\int_A^\infty \exp(-E/kT)dE}.$$

At room temperatures, the penetration of this barrier is unimportant; the separation of the isotopes is small; and the transition state method is satisfactory. At low temperatures the transition state method is inapplicable since most reactions occur by penetration of the barrier. Here the reaction rates are thousands of times faster for the lighter isotope. The above table is in agreement with the calculations of Bell[8] who used an Eckart type of potential barrier. From this table we can make the following observations:[4] At very low temperatures an experimenter would find that a reaction of this nature has an anomalously small steric factor and shows practically no "activation energy." (But at temperatures so low that k_{through} is greater than k_{over}, the rates are so small that they can hardly be measured.) At high temperatures he would obtain an activation energy agreeing with his classical expectations but the steric factor would still be small by a factor of two or three.

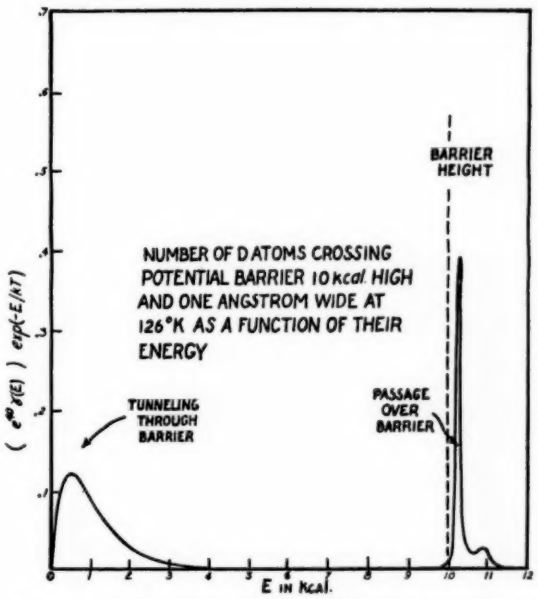
BARRIER HEIGHT
NUMBER OF D ATOMS CROSSING POTENTIAL BARRIER 10 kcal HIGH AND ONE ANGSTROM WIDE AT 126°K AS A FUNCTION OF THEIR ENERGY
TUNNELING THROUGH BARRIER
PASSAGE OVER BARRIER
E IN kcal.

FIG. 7. Relative number of D atoms which succeed in crossing a potential energy barrier 10 kcal. high and 1A wide plotted as a function of their energy. The systems approaching the barrier have the energy distribution corresponding to 126°K.

IV. The Simplest Many-Dimensional Rate Problem—Eyring's Formulation

Reaction rate problems in many dimensions are more complicated than the one-dimensional examples principally because of the interchange of energy between the various degrees of freedom. In this section we consider the simplest of all many-dimensional problems—a straight reaction path along which the motion is slow and perpendicular to which the motion is fast.

If we designate by X the coordinate along the reaction path and x the coordinate perpendicular to the reaction path (considering only one such coordinate x for the sake of simplicity), the potential energy of the system is $U(X, x)$. We

TABLE I.

	T	$\frac{k_{\text{THROUGH}}}{k_{\text{CLASS}}}$	$\frac{k_{\text{OVER}}}{k_{\text{CLASS}}}$	k	k_{CLASS}	k_{TRANS}
H	84°	$1.7\cdot10^{13}$	0.15	$7.1\cdot10^{-5}$	$4.3\cdot10^{-18}$	$3.2\cdot10^{-19}$
	126°	$7.2\cdot10^{4}$	0.22	$1.5\cdot10^{-4}$	$2.1\cdot10^{-9}$	$2.9\cdot10^{-10}$
	252°	0.014	0.35	0.364	1.0	0.39
D	84°	$1.5\cdot10^{8}$	0.22	$4.6\cdot10^{-10}$	$3.0\cdot10^{-18}$	$2.3\cdot10^{-19}$
	126°	0.76	0.26	$1.5\cdot10^{-9}$	$1.5\cdot10^{-9}$	$2.0\cdot10^{-10}$
	252°	0.0023	0.37	0.26	0.707	0.28

denote by x_0 the point x at which $U(X, x)$ assumes its minimum value for a given X. Obviously x_0 is a function of X. $U(X, x)$, as a function of x has approximately the shape of a parabola in the neighborhood of $x=x_0$. If the motion along the reaction path is so slow that the system can vibrate many times in the x direction before it proceeds so far in the direction of X that the curvature of the parabola is changed considerably, the motion perpendicular to the reaction path can be considered as simple harmonic with the frequency $\nu(X)$. The potential energy which is responsible for the motion of the slow coordinate X is then

$$V_n(X)=U(X, x_0)+(n+\tfrac{1}{2})h\nu(X). \quad (20)$$

Here n is the quantum number of the vibration along x. If $V_n(X)$ is a slowly varying function of X, the motion along the reaction path will obey the classical equations of motion.

It is essential in the derivation of Eyring's formulae[1] that the motion in the fast and in the electronic coordinates be adiabatic in the sense that neither the electronic quantum states nor n undergo any changes. We can use the ordinary methods of perturbation theory to obtain the corresponding condition on the velocity, $v=dX/dt$, and on the change in the vibration frequency along the reaction path, $d\nu(X)/dX$,

$$d\nu/dt=vd\nu(X)/dX\ll\nu^2. \quad (21)$$

Here v can be much greater than the velocity corresponding to the average thermal energy since it must be fast enough to permit the crossing of the potential barrier. Thus (21) is more stringent than for the case of motion with ordinary thermal energies of the order of kT.

Under the above conditions, the motion of a system with the vibrational quantum number n will obey classical mechanics and will be governed by the potential (20). Therefore, the number of systems with this vibrational quantum number which react in unit time will be given by (1) into which

$$P_{tn}=\delta \exp(-V_n(X_0)/kT) \quad (22)$$

must be substituted for P_t, where $V_n(X_0)$ is the highest value of $V_n(X)$, corresponding to the activated state.

The total reaction rate is the sum of the rates of all systems in all possible vibrational states. This is

$$\sum_n P_{tn}\bar{v}\gamma/\delta P_i=P_t\bar{v}\gamma/\delta P_i, \quad (23)$$

where

$$P_t=\sum_n P_{tn}=\delta \exp(-V_0(X_0)/kT) \times(1-\exp(-h\nu(X_0)/kT))^{-1}. \quad (24)$$

Thus under these assumptions we are led back to Eq. (1) except that the quantum theoretical probability appears in it, instead of the classical one.

It may be worth while to remark in this connection that if the reflection coefficients are zero and the molecules are distributed before the reaction according to thermal equilibrium, the thermal equilibrium will be maintained throughout the course of the reaction. Consider each vibrational state as forming a separate energy surface with respect to the motion along the reaction path. On the surface characterized by the vibrational quantum number n, the density at any point, X, is given by the barometric formula, $C_n \exp((V_n(\text{initial})-V_n(X))/kT)$. The condition that the systems be at thermal equilibrium initially is that

$$C_n=C \exp((V_0(\text{initial})-V_n(\text{initial}))/kT).$$

From this it follows that the ratio of the density on the nth to that on the zeroth vibrational state is $\exp((V_0(X)-V_n(X))/kT)$ for any value of X.

The consideration of this section shows that it is easy to justify Eyring's formulae with a mechanically sensible transmission coefficient if the coordinates can be divided into some which involve slow motion and others which involve fast motion. The slow motion can be described by classical mechanics. The fast motion can be treated on a par with the motion of the electrons: the corresponding quantum numbers undergo no changes during the reaction. This condition restricts the consideration of this section to potential surfaces where the frequencies along the reaction path change slowly.

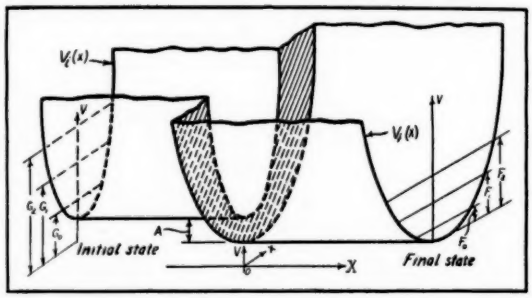

FIG. 8. Two-dimensional potential energy trough with straight reaction path and an abrupt change in the potential. Here the G's are the vibrational energy levels in the initial state and the F's in the final state.

V. ABRUPT CHANGE OF POTENTIAL ENERGY ON TWO-DIMENSIONAL SURFACES

The difficulty of solving partial differential equations restricts the number of many-dimensional rate problems which we can treat accurately. In this section we consider examples in which the reaction path is straight and the change in the potential occurs in a very short distance. It would also be desirable to consider the effect of curvature in the reaction path. The potential energy surfaces are constructed so that the Schrödinger equation is separable in each of a number of regions. In each region, the wave functions are obtained as solutions of ordinary(one-dimensional) differential equations. The wave functions are then pieced together so that the functions and their derivatives are continuous at the boundaries of every two regions. This is carried out by matrix methods and the complete mathematical treatment is given in the appendix.

Let us consider an energy surface similar to that shown in Fig. 8. For negative X, the potential energy is $V_i(X)=A+a_i x^2$; for positive X, the potential energy is $V_f(X)=a_f x^2$. This surface is the two-dimensional analog of the potential drop of Section 3. Eq. (8) enables us to obtain the average transmission coefficient from the reflection coefficients at two energy drops similar to that of Fig. 8. The case in which the energy of the system is large compared with the vibrational energy of any of the levels in the final state to which the waves are likely to be transmitted is particularly easy to treat.

The vibrational quantum number of the reflected systems can differ, to the approximation used in the appendix, only by 0 or ± 2 from the vibrational quantum number of the incident systems. Eqs. (36) and (40) of the Appendix show that even the change by ± 2 is quite improbable as ϵ is always a rather small quantity. The transmitted waves can have a vibrational quantum number differing from that in the initial state by an even number. In Fig. 9, we have plotted the probabilities of reflection and transmission into states with different vibrational quantum numbers. One sees by comparison with Fig. 4, that the reflection coefficient is rather similar to that of a system with equal translational energy in a one-dimensional problem. One sees, furthermore, that the vibrational quantum number has a marked persistence even in this case of an abrupt potential change. This means that the vibrational energy increases if the frequency is larger after the drop, and decreases in the opposite case. The changes in the vibrational frequency, inasmuch as they occur, have a tendency to counteract this. Thus the vibrational quantum number is more likely to decrease if the vibration is stiffer after the drop and is more likely to increase in the opposite case. A more detailed discussion is given at the end of the Appendix.

The persistence of the vibrational quantum number is doubtless in close connection with the slowness with which the equilibrium distribution of vibrations is established. At higher vibrational quantum numbers changes in the vibrational quantum number become more probable which is also in qualitative agreement with experiment.[9]

For the study of reaction rates, the reflection coefficients are most important. It is seen that in the case investigated here—large kinetic energy in the final state—these reflection coefficients are not increased over the value they assume in a similar one-dimensional problem. This leads to the conclusion that the transmission coefficient is even in this case not far from unity and Eyring's well-known formulae remain applicable. It would be desirable to obtain a more general solution of the problem considered in this section than that given in the Appendix and we intend to return to this question at a later time.

[9] Cf. F. Patat, Zeits. f. Elektrochem. **42**, 265 (1936).

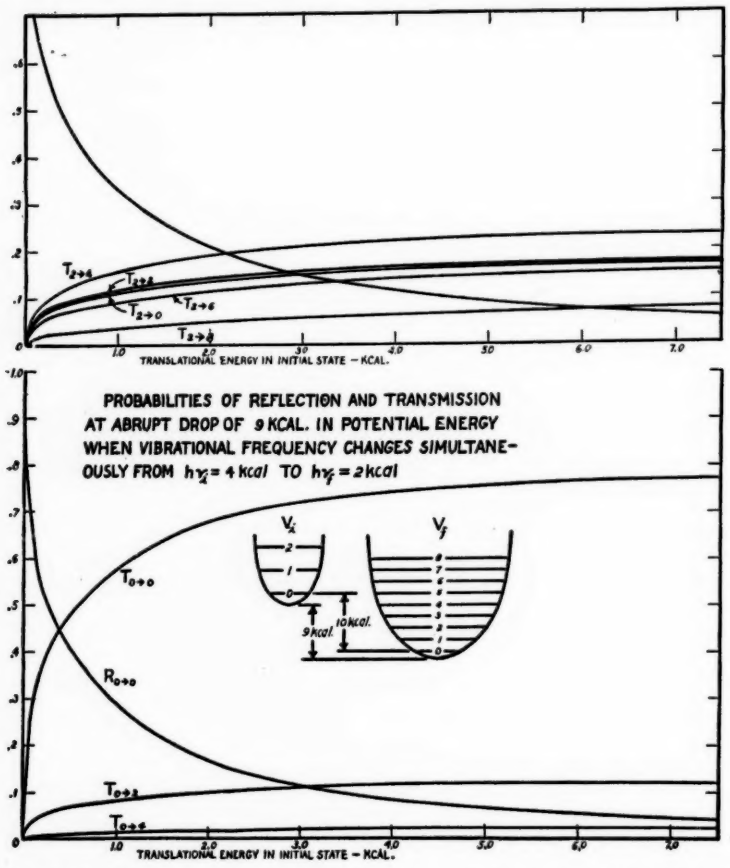
TRANSLATIONAL ENERGY IN INITIAL STATE – KCAL.
PROBABILITIES OF REFLECTION AND TRANSMISSION AT ABRUPT DROP OF 9 KCAL. IN POTENTIAL ENERGY WHEN VIBRATIONAL FREQUENCY CHANGES SIMULTANEOUSLY FROM $h\nu_i = 4$ kcal TO $h\nu_f = 2$ kcal
V_i
V_f
9 kcal.
10 kcal.
$T_{0\to 0}$
$R_{0\to 0}$
$T_{0\to 2}$
$T_{0\to 4}$
TRANSLATIONAL ENERGY IN INITIAL STATE – KCAL.

FIG. 9. Probabilities of reflection and of transmission at an abrupt potential drop of 9 kcal. when the vibrational frequency changes simultaneously from $h\nu_i = 4$ kcal. to $h\nu_f = 2$ kcal. The lower curves are for systems initially in the zeroth vibrational state; the upper curves are for systems initially in the 2nd vibrational state.

APPENDIX

Calculation of transmission and reflection coefficients for many dimensional problems

Let us denote by X the coordinate along the reaction path and by x the coordinate (or coordinates) perpendicular to it. For $X<0$ the potential energy is $V_i(x)$; for $X>0$ it is $V_f(x)$. The characteristic functions and characteristic values of the Schrödinger equation $H_i\psi = I\psi$ with the potential $V_i(x)$ shall be $\psi_\kappa(x)$ and I_κ, those of the Schrödinger equation $H_f\varphi = F\varphi$ with the potential $V_f(x)$ will be $\varphi_k(x)$ and F_k. Greek letters as subscripts refer to the initial state, roman letters to the final state. Expanding the φ in terms of the ψ we obtain

$$\varphi_k(x) = \sum_\kappa u_{k\kappa}\psi_\kappa(x) \tag{26}$$

and u is a unitary matrix

$$(u^{-1})_{\kappa k} = u_{k\kappa}^*. \tag{27}$$

We shall consider an incident wave from the left having the form $\psi_\kappa(x)\exp(2i\pi q_\kappa X/h)$. It will give rise to a reflected beam in which the atoms have all possible quantum numbers λ for their motion in the x direction. Thus the wave function for $X<0$ becomes

$$\psi_\kappa(x)\exp(2\pi i q_\kappa X/h) + \sum_\lambda R_{\kappa\lambda}\psi_\lambda(x)\exp(-2\pi i q_\lambda X/h) \tag{28}$$

with

$$q_\kappa^2/2m + I_\kappa = E, \tag{28a}$$

where E is the total energy of the system. For

$X>0$ we have only an outgoing wave

$$\sum_k T_{\kappa k}\varphi_k(x)\exp(2\pi i p_k X/h) = \sum_{k\lambda} T_{\kappa k}u_{k\lambda}\psi_\lambda(x)\exp(2\pi i p_k X/h), \quad (29)$$

where again

$$p_k^2/2m + F_k = E. \quad (29a)$$

Naturally, the p_κ and q_k with high quantum numbers κ and k will be imaginary. The corresponding terms represent local disturbances in the neighborhood of the discontinuity. The imaginary p and q, must be, if divided by i, positive. Terms with imaginary momenta of the opposite sign of p or q would correspond to waves which have progressively greater amplitudes as we depart from the discontinuity. The total number of systems with quantum number λ reflected in unit time by the discontinuity is $R_{\kappa\to\lambda} = |R_{\kappa\lambda}|^2 q_\lambda/m$, if q_λ is real (there is of course no reflected wave with imaginary q_λ). Similarly, the total number of systems transmitted in unit time with the quantum number k into the final states is $T_{\kappa\to k} = |T_{\kappa k}|^2 p_k/m$ if p_k is real, zero if p_k is imaginary. There are q_κ/m systems incident in unit time.[10]

Both the wave function and its derivative must be continuous at $X=0$. Comparing the coefficients of $\psi_\lambda(x)$ of Eqs. (28) and (29) and of their derivatives this gives:

$$\delta_{\kappa\lambda} + R_{\kappa\lambda} = \sum_k T_{\kappa k}u_{k\lambda}, \quad (30)$$

$$\delta_{\kappa\lambda}q_\kappa - R_{\kappa\lambda}q_\lambda = \sum_k T_{\kappa k}u_{k\lambda}p_k. \quad (30a)$$

The formal solution of these equations can be obtained by matrix algebra. We can write for (30) and (30a)

$$1 + R = Tu, \quad (31)$$

$$q - Rq = Tpu. \quad (31a)$$

Here 1 is the unit matrix, p and q diagonal matrices while R, T and u are general matrices. We have, from (31) and (31a), $T = (1+R)u^{-1} = (1-R)qu^{-1}p^{-1}$ and hence, with $\zeta = qu^{-1}p^{-1}u$,

$$R = (\zeta-1)(\zeta+1)^{-1}; \qquad T = 2\zeta(\zeta+1)^{-1}u^{-1}. \quad (32)$$

We can use (32) to verify that the total number of incident systems is equal to the number of reflected and transmitted systems. The reflection and transmission matrices $\bar{R}$ and $\bar{T}$ for the problem in which the potential is V_f in the initial and V_i in the final state, can be calculated from R and T

$$\bar{R} = -uRu^{-1}; \qquad \bar{T} = u(1-R). \quad (32a)$$

Naturally, (32) represents only a formal solution of our problem, and the matrix elements of R and T still remain to be calculated. We shall obtain them for the special case in which the total energy E is very large compared to the energies F_k of the levels to which there is an appreciable transition. This means that in the final state the translational energy $p_k^2/2m \gg F_k$ will be large compared with the vibrational energy, although this need not be true for the initial state.

In this case $F_k \ll E$ and[11] we can write, denoting by f the diagonal matrix with the diagonal elements F_k,

$$\zeta = qu^{-1}p^{-1}u = qu^{-1}(2mE)^{-\frac{1}{2}}(1+f/2E)u = \zeta_0+\zeta_1, \quad (34)$$

where we have with $P=(2mE)^{\frac{1}{2}}$

$$\zeta_0 = P^{-1}q; \quad \zeta_1 = \tfrac{1}{2}P^{-1}E^{-1}qu^{-1}fu \quad (34a)$$

and ζ_1 is small compared with ζ_0. Now we can write, up to terms of second order in ζ_1

$$\begin{aligned} R &= (\zeta_0-1+\zeta_1)(\zeta_0+1+\zeta_1)^{-1} \\ &= (\zeta_0-1+\zeta_1)(\zeta_0+1)^{-1}[(\zeta_0+1+\zeta_1)(\zeta_0+1)^{-1}]^{-1} \\ &= (\zeta_0-1+\zeta_1)(\zeta_0+1)^{-1}[1-\zeta_1(\zeta_0+1)^{-1}] \\ &= (\zeta_0-1)(\zeta_0+1)^{-1}+2(\zeta_0+1)^{-1}\zeta_1(\zeta_0+1)^{-1}. \end{aligned} \quad (35)$$

Hence

$$R_{\kappa\lambda} = \frac{q_\kappa - P}{q_\kappa + P}\delta_{\kappa\lambda} + \frac{PE^{-1}q_\kappa F_{\kappa\lambda}}{(q_\kappa+P)(q_\lambda+P)}, \quad (36)$$

where

$$F_{\kappa\lambda} = \sum_k u_{k\kappa}^* F_k u_{k\lambda} = \int \psi_\kappa^* H_f \psi_\lambda.$$

For the amplitude of the wave reflected without any change in the vibrational quantum number,

[10] The matrix method for problems of atomic scattering has been initiated by J. A. Wheeler, Phys. Rev. **52**, 1107 (1937).

[11] In this calculation, the zero of the energy is at the bottom of the potential curve $V_f(x)$. E and P are numbers, the other symbols matrices.

the expression

$$R_{\kappa\kappa}=(q_\kappa-p_\kappa')(q_\kappa+p_\kappa')^{-1};\ p_\kappa'^2/2m+F_{\kappa\kappa}=E \quad (37)$$

is correct up to second-order terms in F. This shows a marked analogy to (15) with the difference, however, that p_κ' enters instead of p_κ. The former is smaller than the latter, at least for $\kappa=1$, as $F_{11}>F_1$. Hence, the reflection without change of the vibrational quantum number is smaller in the two-dimensional case than the whole reflection in the one-dimensional case. In order to calculate the $F_{\kappa\lambda}$ we can note that

$$F_{\kappa\lambda}=\int\psi_\kappa^*H_f\psi_\lambda=\int\psi_\kappa^*H_i\psi_\lambda-\int\psi_\kappa^*(V_i-V_f)\psi_\lambda$$
$$=I_\kappa\delta_{\kappa\lambda}-(V_i-V_f)_{\kappa\lambda}. \quad (38)$$

If V_i and V_f have both the potential of a simple harmonic oscillator,

$$V_i=A+2\pi^2m\nu_i^2x^2;\qquad V_f=2\pi^2m\nu_f^2x^2, \quad (39)$$

(36) and (38) show that the vibrational quantum number can change only by 0 or ±2 in our approximation. Then

$$(V_i-V_f)_{\kappa\kappa}=A+\tfrac{1}{2}\epsilon h\nu_i(\kappa+\tfrac{1}{2}),$$
$$(V_i-V_f)_{\kappa\,\kappa+2}=(V_i-V_f)_{\kappa+2\,\kappa} \quad (40)$$
$$=\tfrac{1}{2}\epsilon h\nu_i(\kappa+1)^{\frac{1}{2}}(\kappa+2)^{\frac{1}{2}}$$

with $\epsilon=(\nu_i^2-\nu_f^2)/\nu_i^2$. There is no change whatever in the vibrational quantum number if the frequencies in initial and final states are equal. In general, the probability of a change increases with increasing vibrational energy in the initial state, and also with increasing translational energy as long as the latter remains small compared with the total drop A in the potential.[12]

[12] It should be remembered that the probability of reflection is $|R_{\kappa\lambda}|^2q_\lambda/q_\kappa$, not $R_{\kappa\lambda}$.

For the transmission matrix we obtain from (31)

$$T_{\kappa k}=\sum_\lambda(\delta_{\kappa\lambda}+R_{\kappa\lambda})u_{k\lambda}^*$$
$$=\frac{2q_\kappa}{q_\kappa+P}u_{k\kappa}^*+\sum_\lambda\frac{PE^{-1}q_\kappa F_{\kappa\lambda}u_{k\lambda}^*}{(q_\kappa+P)(q_\lambda+P)}. \quad (41)$$

The second term contains the factor F/E and is much smaller than the first. We shall evaluate (41) also for the potentials (39). In this case $T_{\kappa k}$ will be zero unless the change $(k-\kappa)$ of the vibrational quantum number is even. This is because both $F_{\kappa\lambda}$ and $u_{k\kappa}$ vanish, unless the difference of their two indices is even. The first few u are

$$u_{00}=(1-\epsilon)^{\frac{1}{2}}(1-\epsilon+\tfrac{1}{4}\epsilon^2)^{-\frac{1}{2}},$$
$$u_{02}=-u_{20}=2^{-\frac{1}{2}}u_{00}\epsilon(2-\epsilon)^{-1}, \quad (42)$$
$$u_{22}=u_{00}(1-\epsilon-\tfrac{1}{8}\epsilon^2)(1-\epsilon+\tfrac{1}{4}\epsilon^2)^{-1}.$$

If the change in vibrational frequency is not too large, ϵ will be small. Under these conditions, at least for low values of the indices, the diagonal elements of u are nearly 1. The off-diagonal elements are much smaller, as $u_{k\kappa}$ contains the $\frac{1}{2}(k-\kappa)'$th power of ϵ. Thus the probability for a change in κ is small. For large values of the quantum numbers, the vibrational energy in the final state covers a wider range. In the classical region, it extends from the vibrational energy in the initial state I_v to $I_v(1-\epsilon)$. Its mean value is still very nearly the same as if there was no change in vibrational quantum number: it is $I_v(1-\frac{1}{2}\epsilon)$ instead of $I_v(1-\epsilon)^{\frac{1}{2}}$.

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The N−H Harmonic Bands of Pyrrole at λ9900, and the Structure of the Pyrrole Molecule

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(Received June 24, 1939)

IN their study of the infra-red absorption of organic substances in carbon tetrachloride solution Wulf and Liddel[1] found that the strong second harmonic N−H band of pyrrole is accompanied by a weak satellite which lies approximately 50 cm^{-1} to the long wave side and has roughly one-twentieth the intensity of the main band. The main band has been attributed by Pauling[2] to a planar pyrrole molecule and the weak satellite to a second molecular species in which the imino hydrogen lies out of the plane of the other atoms.

In a study of pyrrole vapor in the third harmonic region M. Freyman[3] found three components in the N−H absorption; a strong band at λ9818, a much weaker one at λ9890, and a very faint band at λ9961, respectively. These Freyman attributed to three molecular species.

Since this explanation did not appear very plausible it has seemed worth while to make further studies of the third harmonic region. Consequently the N−H absorption of pyrrole vapor has been photographed both with low and high dispersion and at two temperatures (150° and 250°C). In the low dispersion studies it was observed that with rise in temperature the λ9890 and λ9961 bands show moderate and large increases in intensity, respectively, relative to the λ9818 band. From this fact it is clear that while the main band presumably arises from absorption from the ground level the two subsidiary maxima must involve absorption from two *different* excited states. That these states do not, however, correspond to different geometrical configurations of the molecule but merely to vibrational excitation is shown by the high dispersion studies.

It was not possible to photograph the faint λ9961 band under high dispersion but the other two bands showed very characteristic envelopes which were apparently identical except for the difference in intensity. As shown in the figure they consist of *P* and *R* branches and narrow *Q* branches which are not very strong but have in both cases the same intensity relative to the rest of the band. Since the intensity of the *Q* branch will be very sensitive to the direction of change of electric moment in the N−H vibration,[4] and consequently to the orientation of the N−H bond it seems quite certain that the two bands just mentioned originate in one and the same molecular species. Consequently it is reasonable to ascribe the λ9890 band to a transition in which some low frequency vibration is excited in both lower and upper levels. The equality of spacings between the bands and the intensity ratios indicates that the λ9961 component is the third member of the sequence.

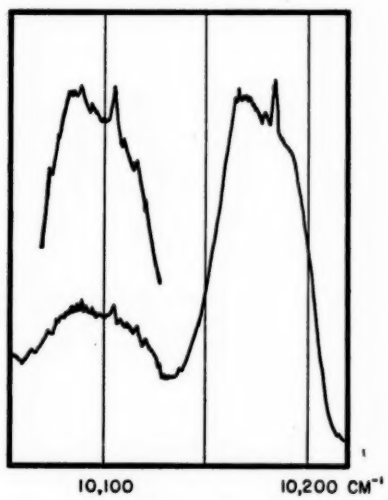

FIG. 1. Microphotometer curve of the third harmonic N−H bands in pyrrole vapor taken under high dispersion at 250°C. The upper curve at the left shows the second member of the band sequence recorded with increased microphotometer sensitivity for better comparison with the main band.

[1] Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).
[2] L. Pauling, J. Am. Chem. Soc. **53**, 94 (1936).
[3] M. Freyman, Comptes rendus **205**, 852 (1937); Ann. de Chemie **11**, 11 (1939).
[4] For a discussion of band envelopes of unsymmetrical molecules see: R. M. Badger and L. R. Zumwalt, J. Chem. Phys. **6**, 711 (1938).

Such sequences, with two or more members of appreciable intensity, are of general occurrence in molecules with low frequency vibrations though in most cases the separation between members is too small for them to be detected in incompletely resolved bands. The fact that in pyrrole one such sequence has been resolved implies an unusually large interaction between the N−H valence vibration and some other mode of motion of low frequency. The intensity ratios and also the temperature effect indicate that the second vibration has a frequency in the neighborhood of 650 cm^{-1}. The large interaction with the N−H valence vibration suggests that it involves some bending motion of the N−H bond with respect to the rest of the molecule.

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LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Erratum and Addendum: Vibration Spectra and Molecular Structure. VII. Further Infra-Red Studies on the Vapors of Some Carboxylic Acids

(J. Chem. Phys. **7**, 460 (1939))

In a publication with the above title we reported a spectroscopic determination of the heat of association of propionic acid-*d* and remarked erroneously that our calculation of the heat of association was independent of the absorption constant. This remark would be true if the quantity P_D/P, which occurs in the formula

$$K_p=\frac{(1-P_D/P)^2P}{P_D/P},$$

is maintained at a constant value by adjusting the temperature and pressure. In this case a knowledge of the true absorption constant would be unnecessary. In the determination reported P_D/P was not always kept constant and therefore a value of the absorption constant has to be assumed. If the absorption constant assumed for these calculations differs from the true value by more than about 17 percent, the curve for $\log_{10} K_p$ *vs.* $1/T$ deviates from a straight line by a measurable amount. However, if the absorption constant differs by less than about 17 percent, the only effect noticeable above the scattering of points due to experimental error would be a change of slope of the straight line by about 5 percent.

Since the data we have obtained for propionic acid-*d* seem to fit a straight line, it would seem that the value of the absorption constant we have assumed for propionic acid-*d* cannot differ form the true value by more than about 17 percent. It now becomes necessary to change the probable error in the heat of association of propionic acid-*d* by about 350 calories per mole per bond because of a possible error in the absorption constant. In the case of acetic acid-*d* the absorption constant was calculated with the aid of MacDougall's data and since our results gave a straight line consistent with that of MacDougall we feel that no revision is necessary.

It is a pleasure to thank Professor E. Teller for an interesting discussion.

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An Electronic Transition of the Rydberg Series Type in the Absorption Spectra of Hydrocarbons

In an analysis of our experimental results on the absorption spectra of a series of dienes, which will be published shortly, a possible theoretical interpretation of our earlier results on mono-olefins and cyclic hydrocarbons[1, 2] has developed which seems to be of significance in the general study of molecular spectra of polyatomic molecules. The seventeen olefin hydrocarbons which have been examined in this laboratory all show a group of narrow diffuse absorption bands of high intensity in the region between 43,000 and 53,000 cm^{-1} and the position of the first band in each compound is determined by the number of alkyl groups bound to the carbon atoms of the double bond but is independent of the nature of the group. There is a progressive shift toward the visible as the number of alkyl groups is increased. If the position of this band for each compound is plotted as a function of the number of such alkyl groups and the corresponding value for ethylene with no substituent is taken as 57,320 cm^{-1}, measured by Price,[3] the result is very nearly a straight line. This relationship was used to justify our assumption that the bands represented an analogous, electronic transition in ethylene and in its derivatives. The electronic band for ethylene was shown by Price to be the first member of a Rydberg series but the diffuseness of the bands in the ethylene derivatives and the variable intensity factors made it difficult to confirm a similar assignment for the more complex hydrocarbons. The results of our study of dienes have shown, however, that the sharpness as well as the relative intensities of the bands is modified profoundly where they are superimposed on a region of continuous absorption due to other electronic transitions. It seems quite certain therefore that these first bands in the Schumann region, which are found in the spectra of all the olefins, constitute the first electronic band system of a Rydberg series which is superimposed on a continuous band of high intensity which, for most of the olefins, has a maximum about 57,000 cm^{-1}. On the basis of theoretical considerations this latter band in the ethylene derivatives is assigned by Mulliken to a charge-transfer transition ($N \rightarrow V$) characteristic of this type of homopolar molecule.[4]

An important corollary of the identification of the shallow bands of the olefins with a Rydberg series transition, is its application to the interpretation of the benzene spectrum. The parallelism in position between the first bands in the Schumann region of all the hydrocarbons both aliphatic and cyclic having the grouping $C-CH=CH-C$ has been pointed out[2] and the extraordinary similarity between the bands of cyclohexene and *cis*-butene-2[5] is more readily understood if the electronic transition is of the Rydberg series type where the electron concerned is nonbonding and the energy of the transition would be dependent primarily upon the effective nuclear charge of the carbon atom. This effective charge would be strongly influenced and probably determined by the number and arrangement of hydrogen and carbon atoms directly bound to the carbon atoms of the double bond and therefore the energy of excitation of a nonbonding electron would be nearly the same in all hydrocarbons containing a similar grouping. The identification of the group of strong bands between 48,800 and 54,000 cm^{-1} in the spectrum of benzene as belonging to the first member of a Rydberg series which may be superimposed upon another electronic transition, predicted by Goeppert-Mayer and Sklar[6] as a weak band due to a forbidden electronic transition would explain the anomalous intensity relationship.

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July 14, 1939.

[1] E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936).
[2] E. P. Carr and H. Stücklen, J. Chem. Phys. **6**, 55 (1938).
[3] W. C. Price, Phys. Rev. **47**, 444 (1935).
[4] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).
[5] E. P. Carr and H. Stücklen, J. Am. Chem. Soc. **59**, 2138 (1937).
[6] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

Activated Adsorption of Nitrogen on Iron at 23° and 100°C, and Ammonia Synthesis

During the recent symposium on "Fundamentals of Heterogeneous Catalysis" (A.C.S. Meeting, Baltimore) ammonia synthetic catalysts were discussed from various angles. In the light of these discussions, it appeared to be of great interest to investigate the adsorption of nitrogen on evaporated iron films. Technique of production of such films was discussed by one of the writers during the same symposium and, among others, adsorption measurements were presented for various gases on nickel films.

As in the case of nickel, very rapid chemisorption was observed for hydrogen on iron at room temperature. In contrast to nickel, however, iron also adsorbs nitrogen at room temperature. The amount adsorbed is roughly one-fifth of the hydrogen adsorption. Whereas, the hydrogen adsorption on iron is practically instantaneous, considerable time is required for the activated adsorption of nitrogen at room temperature. The remaining four-fifths of the surface can be covered with hydrogen bringing the total adsorption to the same number of molecules as in the case of hydrogen alone. Apparently no interaction between the co-adsorbed gases takes place. If the iron film is heated to 100°C, it sinters and the amount of hydrogen it will take up after cooling to room temperature is about 80 percent of that of a film evaporated at room temperature. On such a sintered catalyst, much less than one-fifth of the available surface (as measured by hydrogen adsorption) may be covered with nitrogen at room temperature. If, however, the nitrogen is admitted to the iron film at 100°C again about one-fifth of the total available surface is covered by nitrogen. The rate of this adsorption is considerably faster than that at room temperature on the unsintered catalyst. Attempts to produce ammonia in the gas phase by, for instance, heating the iron film on which nitrogen is actively adsorbed in a hydrogen atmosphere have so far failed. If, however, the iron films on which nitrogen was adsorbed at room temperature or at 100°C are dissolved in hydrochloric acid, the presence of ammonia can be readily shown by distilling with alkali and testing by Nestler's reagent. The

amount of ammonia found was roughly in quantitative agreement with the amount of nitrogen adsorbed. This ammonia synthesis takes place independent of the presence of free or adsorbed hydrogen. No nitrogen is adsorbed either at room temperature or at 100°C and consequently no ammonia is formed if hydrogen is admitted to the iron film first.

A detailed account and discussion of this work will be published in due time. Thanks are due to Messrs. W. A. Cole and A. B. Bullock for help with the experiments and analyses.

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Shell Development Company,
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July 12, 1939.

Ultrasonic Velocities in and Adiabatic Compressibilities of Mixtures of Acetic Acid and Water

Using the method of Debye and Sears[1] and of Lucas and Biquard,[1] we have measured the velocities of ultrasonic waves of a frequency of 7.4 megacycles per second, at 25°C, in mixtures of varying concentration of acetic acid and water. The trough containing the liquid was mounted on the prism table of a spectrometer to facilitate the measurement of the angle of diffraction of the light. Since the mixtures are electrically conducting, the piezoquartz was immersed in an inner vessel containing xylene. The waves were transmitted through a mica window to the outer vessel containing the conducting liquid. The frequency of the electrical oscillator was measured with a General Radio, 724-A, frequency meter. The adiabatic compressibility β was calculated by means of the equation $v=(1/\rho\beta)^{\frac{1}{2}}$, in which v is the measured velocity of the ultrasonic waves and ρ is the density of the liquid. This equation gives β in dyne^{-1}; in the values recorded below β is in atmos.$^{-1}$ A sodium vapor lamp was used as a source of monochromatic light. The glacial acetic acid used had a purity of 99.5 percent; it was mixed with distilled water to get the desired concentrations. The results are represented in Fig. 1, which shows that the velocity of the supersonic waves reach a maximum at about 30 percent concentration, by weight, of acetic acid, and that the compressibility has a minimum at this concentration. The variations in ultrasonic velocities and adiabatic compressibilities are somewhat similar to the well-known variations in the density and index of refraction of mixtures of acetic acid and water.

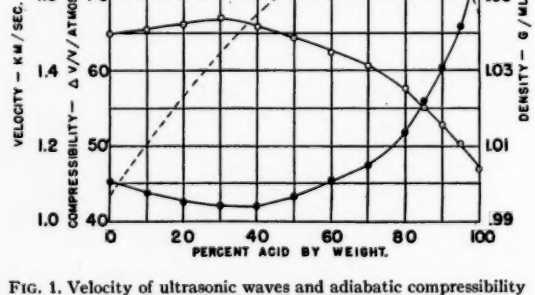

FIG. 1. Velocity of ultrasonic waves and adiabatic compressibility in aqueous solutions of acetic acid.

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The Ohio State University,
Columbus, Ohio,
June 29, 1939.

[1] L. Bergmann, *Ultrasonics* (John Wiley & Sons, 1938), p. 63.

Raman Spectra of Deuterium Substituted Guanidine and Urea

In continuation of earlier work on the Raman spectra of guanidine and urea,[1] we have determined the effect of completely substituting deuterium for hydrogen in the NH_2 groups of these compounds, and have also repeated the earlier measurements on ordinary guanidine and urea. The results are tabulated below. Lines marked *P* are definitely polarized; those marked *D* are probably depolarized.[2]

Guanidonium Chloride

$C(NH_2)_3^+ Cl^-$ in H_2O		$C(ND_2)_3^+ Cl^-$ in D_2O	
536(4*b*)	*D*	459(3)	*D*
1015(8)	*P*	921(8)	*P*
1462(0*vb*)	?	1193(1*b*)	*D*
1565(2*vb*)	*D*	1278(1)	*P*
1670(1*vb*)	?	2127(0?)	—
3212(3*b*)	—	2374(6)	*P*(D_2O?)
3290(3*b*)	—	2433(6)	*P*
3360–3471(H_2O)		2496–2591(6)(D_2O)	

Urea

$CO(NH_2)_2$ in H_2O		$CO(ND_2)_2$ in D_2O	
534(2)	*D*	458(1)	*D*
601(2)	*D*	548(1)	*D*
1008(10)	*P*	890(5)	*P*
1167(4)	*P*	997(6)	*P*
1478(2*b*)	*D*	1049(1)	?
1604(4*b*)	*P*?	1164(1)	*D*
1680(3*b*)	*P*	1201(1*b*)	?
3235(5*b*)	*P*	1247(3)	*P*
3385(6*vb*)	*P*	1613(3*b*)	*P*
3496(5*b*)	*D*	2421(5*vb*)	*P*
		2506(3)	*P*?
		2603(3)	*D*

A detailed analysis of the data will be given later; we may call attention now, however, to the general parallelism of our data on $CO(NH_2)_2$ and $CO(ND_2)_2$ and the data of Engler[3] on $CO(CH_3)_2$ and $CO(CD_3)_2$.

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Harvard Medical School,
Boston, Massachusetts,
July 5, 1939.

[1] J. T. Edsall, J. Chem. Phys. **4**, 1 (1936); J. Phys. Chem. **41**, 133 (1937); see also R. Ananthakrishnan, Proc. Ind. Acad. Sci. (**A**)**5**, 200 (1937).
[2] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938).
[3] W. Engler, Zeits. f. physik. Chemie (**B**)**32**, 471 (1936).

Reactions Involving Hydrogen and the Hydrocarbons*

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(Received April 24, 1939)

The activation energies of the reactions $H+CH_4=CH_3+H_2$ (1) and $D+CH_4=CH_3D+H$ (2) have been calculated by using the semi-empirical method in combination with the treatment of directed valence used by Van Vleck and Voge. The activation energies for reactions (1) and (2) were found to be 9.5 kcal. and 37 kcal. This result agrees with the prediction of 40 kcal. of Rice and Teller for reaction (2). In addition it is found that the energy surface corresponding to the reaction $H+CH_4$ contains a basin 8 kcal. deep corresponding to a stable CH_3-H-H molecule. The rapid recombination of H atoms in the presence of methane, observed by Farkas and Melville is interpreted in terms of this CH_3-H-H intermediate. The experimental data on the reactions of hydrogen and deuterium atoms with hydrocarbons have been reinterpreted in terms of atom-cracking reactions of the type $D+C_2H_6\rightarrow C_2H_5D\rightarrow CH_3D+CH_3$.

INTRODUCTION

THE elucidation of the mechanism of reactions involving hydrocarbons and hydrogen requires the consideration of a bewildering variety of possible reactions. In order to be able to rule out some of the possibilities we have calculated the activation energies of some elementary reactions using the semi-empirical method combined with the theory of directed valence. We have also discussed these reactions from the standpoint of the theory of absolute reaction rates. These considerations lead to a definite point of view with respect to a variety of reaction mechanisms and so serve to illustrate the possibilities and limitations of our present theoretical methods.

THE METHANE-HYDROGEN REACTIONS

The potential surface for the reaction between methane and a hydrogen atom was calculated as a three-electron problem for two of the possible mechanisms. The nine-electron problem was then solved in order to determine whether the potential surface would be appreciably altered by the additional resonance so introduced.

The carbon and hydrogen orbitals in the methane molecule are designated by the letters *a*----*h* as indicated in Fig. 1. The orbital on the fifth hydrogen atom is designated by *i*. In the following calculations the hydrogen atom was assumed to approach along one of the C−H bond directions (i.e., the reaction complex always

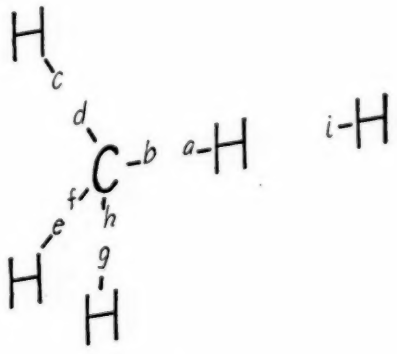

FIG. 1.

* This paper and the eighteen papers which follow it (ten in this issue and eight in the September issue) were presented at a symposium on "The Kinetics of Homogeneous Gas Reactions" at the University of Wisconsin, Madison, Wisconsin, June 20–22, 1939. This symposium was arranged jointly by the Division of Physical and Inorganic Chemistry of the American Chemical Society and the University of Wisconsin cooperating with Section C of the American Association for the Advancement of Science. The symposium committee for the Division of Physical and Inorganic Chemistry consisted of George Scatchard, chairman, E. J. Cohn, Farrington Daniels, H. Eyring, J. H. Hildebrand, L. S. Kassel, C. A. Kraus, V. K. LaMer, P. A. Leighton, and S. C. Lind. The symposium committee for the University of Wisconsin consisted of Farrington Daniels, J. O. Hirschfelder, W. E. Roseveare, and John E. Willard.

The committees are glad to acknowledge financial assistance given by the Wisconsin Alumni Research Foundation.

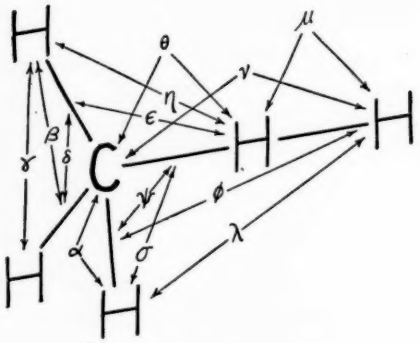

FIG. 2.

possesses at least a threefold axis of symmetry), so that certain of the exchange integrals become equivalent. The exchange integrals are listed in Table I and shown schematically in Fig. 2.

EVALUATION OF THE INTEGRALS

The H−H integrals were evaluated from the H−H Morse curve with $a=1.94$, $r_0=0.74$, $D=108.6$, $\omega_0=43.75$, assuming that the Coulombic integral is 10 percent of the total binding in conformity with Voge's treatment of methane. The C−H integrals were expressed in terms of the more elementary integrals N_{ss}, $N_{s\sigma}$, $N_{\sigma\sigma}$, $N_{\pi\pi}$ defined by Van Vleck,[1] with the values $N_{ss}=2.00$ ev, $N_{s\sigma}=1.69$ ev, $N_{\sigma\sigma}=2.30$ ev, $N_{\pi\pi}=-0.6$ ev as given by Voge.[2]

The carbon orbitals as a function of ω, the angle between the orbitals with their axes, pointing toward the bound H atoms, are given by Van Vleck in the following form.

$$\psi_b{}^c=(1-2\cot^2\omega)^{\frac{1}{2}}\psi(2\sigma_b)-\sqrt{2}\cot\omega\psi(2s),$$

$$\psi_k{}^c=(\tfrac{2}{3}\operatorname{cosec}^2\omega)^{\frac{1}{2}}\psi(2\sigma_k)+(\tfrac{1}{3}-\tfrac{2}{3}\cot^2\omega)^{\frac{1}{2}}\psi(2s), \quad (1)$$

$$k=d,\ f,\ h.$$

TABLE I.

$\alpha=cd=ef=gh$	$\eta=ac=ag=ae$
$\beta=dg=de=cf=fg=eh=ch$	$\varphi=ih=id=if$
$\sigma=bg=be=bc$	$\lambda=ic=ig=ie$
$\gamma=eg=ec=cg$	$\psi=bh=bd=bf$
$\delta=dh=df=fh$	$\mu=ai$
$\epsilon=ah=ad=af$	$\nu=bi$
	$\theta=ab$

[1] J. H. Van Vleck, J. Chem. Phys. **1**, 183 (1933).
[2] H. H. Voge, J. Chem. Phys. **4**, 581 (1936).

The C−H exchange integral between the carbon orbital $\psi_b{}^c$ and a hydrogen orbital is given by

$$\text{(C−H) exchange integral}=2\cot^2\omega N_{ss}$$
$$-2^{\frac{1}{2}}\cot\omega(1-2\cot^2\omega)^{\frac{1}{2}}\cos\chi N_{s\sigma}$$
$$+(1-2\cot^2\omega)\cos^2\chi N_{\sigma\sigma}$$
$$+(1-2\cot^2\omega)\sin^2\chi N_{\pi\pi}, \quad (2)$$

where χ is the angle between the C−H direction and the axis of the carbon orbital.

When the hydrogen atom approaches the methane molecule along the C−H bond direction as in Fig. 3, the integrals θ, ν, σ are obtained from Eq. (2) by placing $\chi=0$, π, ω, respectively. For the case illustrated in Fig. 4, θ, ν, σ are obtained from Eq. (2) by placing $\chi=0$, 0, ω, respectively. Similarly, for C−H exchange integrals involving $\psi_k{}^c$ we obtain

$$\text{(C−H) exchange integral}=(\tfrac{1}{3}-\tfrac{2}{3}\cot^2\omega)N_{ss}$$
$$+2(2/9-4/9\cot^2\omega)^{\frac{1}{2}}\operatorname{cosec}\omega\cos\chi N_{s\sigma}$$
$$+\tfrac{2}{3}\operatorname{cosec}^2\omega(\cos^2\chi N_{\sigma\sigma}+\sin^2\chi N_{\pi\pi}). \quad (3)$$

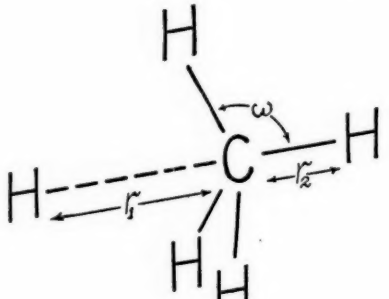

FIG. 3.

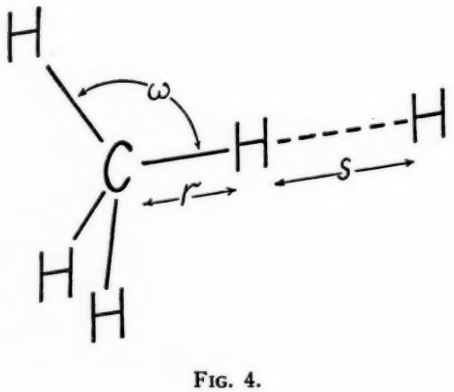

FIG. 4.

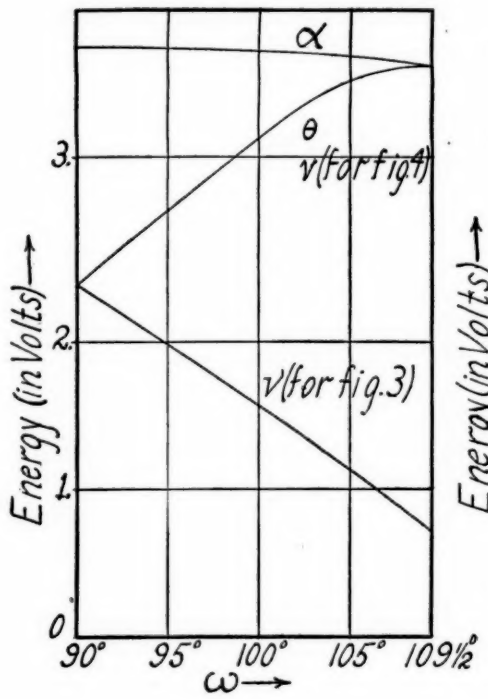

FIG. 5.

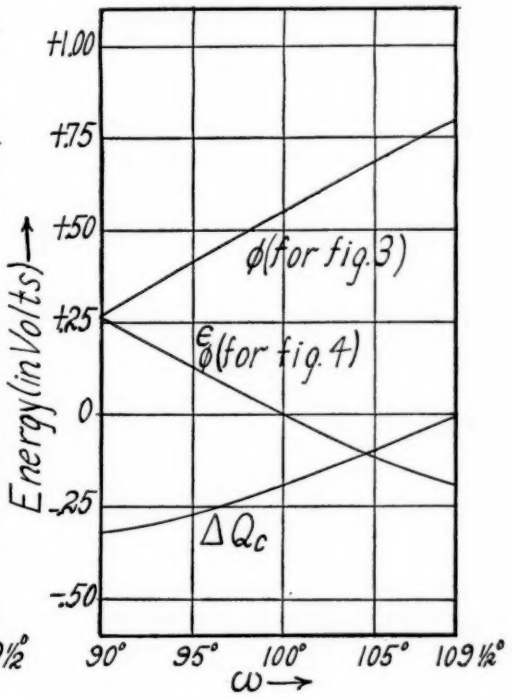

FIG. 6.

For the reaction complex indicated in Fig. 3, we obtain the integrals α, β, ϵ, φ from Eq. (3) by placing $\chi=0$,

$$\cos^{-1}\left(1-3\sin^2\frac{\omega}{2}\right),$$

ω, $\pi-\omega$, respectively. For the reaction complex indicated in Fig. 4, we obtain the integrals α, β, ϵ, φ by placing $\chi=0$,

$$\cos^{-1}\left(1-3\sin^2\frac{\omega}{2}\right),$$

ω, ω, respectively. The exchange integrals ϵ, θ, ν, φ must be considered as a function of the C–H distance. We have assumed that these integrals vary with distance in the same way as does the C–H binding energy as represented by the Morse curve with $r_0=1.12$, $a=1.874$, $\omega_0=2930$, $D=96.46$.

The total Coulombic interaction between the carbon and a hydrogen atom is taken from Voge to be 2.64 ev at the equilibrium distance. Since the carbon atom is spherically symmetric this integral is independent of the valence angle and is assumed also to vary with the distance in the way given by the C–H Morse curve.

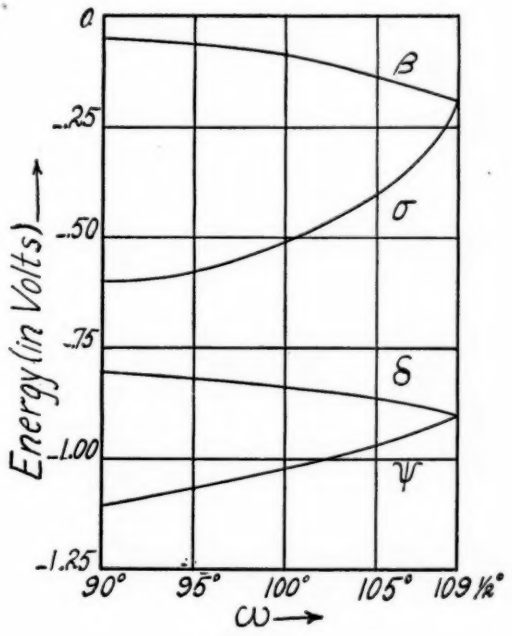

FIG. 7.

The exchange integral ψ between two carbon orbitals can be expressed in terms of the Slater

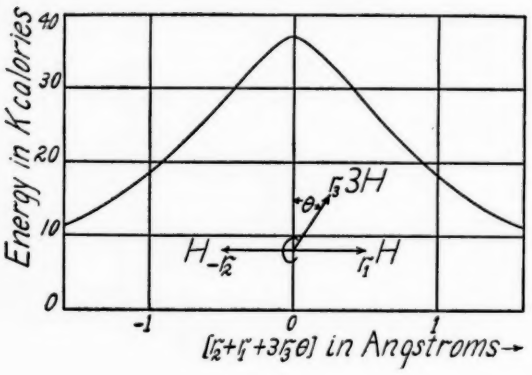

FIG. 8.

parameters F_K and G_K as redefined by Condon and Shortley.[3]

$$\psi=\beta_1^2\beta_2^2F_0(2s,\,2s)+2\alpha_1\alpha_2\beta_1\beta_2\cos\omega F_0(2s,\,2p)$$
$$+\alpha_1^2\alpha_2^2\cos^2\omega F_0(2p,\,2p)$$
$$+(2\alpha_1\alpha_2\beta_1\beta_2\cos\omega+\alpha_2^2\beta_1^2+\alpha_1^2\beta_2^2)$$
$$\times G_1(2s,\,2p)+(3\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_2^2\cos^2\omega)F_2, \quad (4)$$

where $\alpha_1=(1-2\cot^2\omega)^{\frac{1}{2}}$, $\beta_1=-\sqrt{2}\cot\omega$,

$\alpha_2=\sqrt{\frac{2}{3}}\csc\omega$, $\beta_2=(\frac{1}{3}-\frac{2}{3}\cot^2\omega)^{\frac{1}{2}}$.

To obtain the exchange integral δ one replaces α_1 by α_2 and β_1 by β_2 wherever it occurs in the above formula. In addition $\cos\omega$ is replaced by $1-3\sin^2\omega/2$. The values of the F's and G's are also taken from Voge's paper. The intracarbon Coulombic energy Q_c is equal to -88.50 volts for the tetrahedral carbon atom. Since the total energy of the carbon atom in isolation is constant and independent of the valence angle, the Coulomb energy for any valence angle ω may be calculated from the relation $Q_c-3\psi-3\delta=$const. ΔQ_c in Fig. 6 is the difference in Coulombic energy of the carbon atom with a valence angle ω compared with the Coulombic energy of tetrahedral carbon.

The computed values of these integrals for a C−H distance of 1.12A as a function of the valence angle ω are shown in Figs. 5, 6 and 7.

THE REACTION $H+CH_4\rightarrow CH_4+H$ ①

The reaction complex is illustrated in Fig. 3. Considered as a three-electron problem, the energy for any given configuration of the complex is given by

$$E=Q\pm(\tfrac{1}{2}\{(\theta-\nu)^2+(\theta-\mu)^2+(\mu-\nu)^2\})^{\frac{1}{2}}+3\alpha$$
$$-3\beta-\tfrac{3}{2}(\lambda+\varphi+\sigma+\psi+\epsilon+\eta+\gamma+\delta). \quad (5)$$

The potential surface was calculated as a function of r_1, r_2 and ω. From this surface the reaction path was determined, and the energy is plotted in Fig. 8 as a function of the position of the reacting complex along the path of the reaction. Values of the energy for various points along the path are given in Table II. The activated complex is located at $r_1=r_2=1.30$A, $\omega=90°$. The calculated activation energy is 37 kcal. A high activation energy for this reaction is to be expected from the consideration of Rice and Teller,[4] who estimated from spectroscopic data that approximately 40 kcal. are required to change the angle ω in methane from 109° to 90°. Calculations based upon Eq. (5) give a value of 50 kcal. for this process.

THE REACTION $H+CH_4\rightarrow CH_3+H_2$ ②

The reaction complex is illustrated in Fig. 4. Using Eq. (5), the potential surface as shown in Fig. 9 was calculated by minimizing the energy with respect to ω for each value of r and s. The activated complex is at $r=1.17$A, $s=1.40$A, $\omega=105°$. The calculated activation energy for this reaction is 9.5 kcal. The reaction is calculated to be endothermic by 7.4 kcal. The calculation indicates a basin 8 kcal. in depth at $r=1.25$A, $s=0.80$A, $\omega=105°$, corresponding to a stable Coulomb bond between methane and a hydrogen atom.

Numerous workers have investigated the reactions of hydrogen and deuterium atoms with

TABLE II*

r_1	r_2	ω	$3r_2\times(\pi/2-\omega)$	$r_1+r_2+3r_2\times(\pi/2-\omega)$	E
$-\infty$	+1.12A	109½°	−1.14A	$-\infty$	0 kcal.
−1.70A	+1.15A	107°	−1.00	−1.55A	12
−1.40	+1.17	103°	− .69	− .92	20
−1.37	+1.20	97°	− .35	− .52	28
−1.34	+1.25	94°	− .24	− .33	32
−1.30	+1.30	90°	0	0	37

* r_3 is held at 1.12A throughout.

[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929); E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

[4] F. O. Rice and E. Teller, J. Chem. Phys. **6**, 489 (1938).

methane. Thus investigations of the mercury photosensitized substitution of deuterium in methane have yielded a value of 11.7 kcal.[5] for the activation energy of the deuterization reaction. This activation energy calculated from the collision yield was identified with the reaction of $CH_4+D\rightarrow CH_3D+H$. Morikawa, Benedict and Taylor[6] have also calculated an activation energy of 12.5 to 14 kcal. from the collision yield. They suggest that the reaction responsible for the exchange reaction below 200°C may be

$$Hg^*+CH_4\rightarrow CH_3+H+Hg$$

but that in the higher temperature range the reaction $D+CH_4=CH_3+HD$ may occur with an activation energy of $\sim$15 kcal.

Investigations[7] bearing more directly on these reactions were carried out by studying the reactions of deuterium atoms drawn from a Wood's discharge tube with methane. Trenner, Morikawa and Taylor give a value of 15.6 kcal. for the activation energy computed from the collision yield for the reaction

$$CH_4+D\rightarrow CH_3+HD. \qquad (A)$$

Steacie in a more extended investigation obtained a value of 12.9 ± 2 kcal. The experimental activation energy of around 12 kcal. must, then, be identified with that of reaction (A) and is to be compared with the computed value of 9.5 kcal.

It is interesting to note that calculations, made with the hydrogen atom coming up at an angle with the C−H direction, have shown that the activation energy remains constant for the reaction

$$D+CH_4\rightarrow DH+CH_3.$$

That is, the methane behaves as if it were spherically symmetric, any arbitrary direction of approach being almost equally effective within 400 cal. in causing the reaction to take place. In addition, for the activated complex, the C−H distance is very nearly the same as in methane. This, then, justifies the use of the collision theory in the calculation of the activation energy as was done by most investigators of this reaction. It was usual to use a steric factor of 0.1, which is unnecessary with a transmission coefficient of unity. However, the actual diameter of the activated complex is somewhat smaller than the value calculated from kinetic theory, i.e., 3.6×10^{-8} cm as compared with 5.9×10^{-8} cm. This accounts for an apparent steric factor of $(3.6/5.9)^2=0.37$. The fact that all directions are

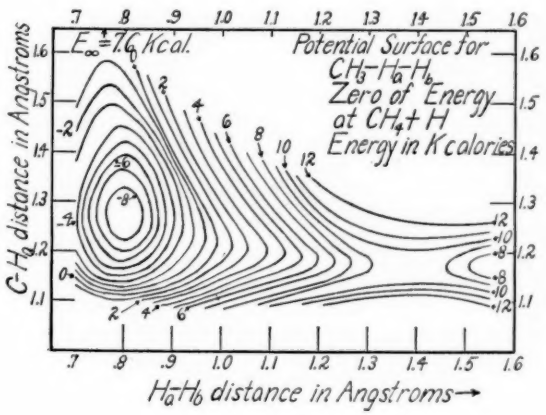

FIG. 9.

not exactly equally effective would introduce another small apparent steric factor. The transmission coefficient should be about $\frac{1}{2}$ since there is a basin on the other side of the saddle point. The steric factor $\frac{1}{10}$ usually used is therefore a very reasonable one.

The back reaction $CH_3+H_2\rightarrow CH_4+H$ has been investigated by numerous authors.[8] Hartel and Polanyi estimate a value of 8 kcal. for the activation energy, Trenner, Morikawa and Taylor give a value of 11 kcal., while Taylor and Rosenblum, from an investigation of the photolysis of acetone in the presence of hydrogen, give a value of 11 ± 2 kcal. We see then that the experimental value for the heat of reaction (1) is of the order of 3 kcal. as compared with the theoretical value of 7.6 kcal.

THE RESONANCE ENERGY

We have solved the nine-electron problem with trigonal symmetry to investigate the accu-

[5] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).
[6] K. Morikawa, W. S. Benedict and H. S. Taylor, J. Chem. Phys. **5**, 212 (1937).
[7] K. H. Geib and E. W. R. Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935), Trans. Roy. Soc. Can. III **29**, 91 (1935); N. R. Trenner, K. Morikawa and H. S. Taylor, J. Chem. Phys. **5**, 203 (1937); E. W. R. Steacie, Can. J. Research **15B**, 264 (1937).
[8] H. v. Hartel and M. Polanyi, Zeits. f. physik. Chemie **11B** 97 (1930); H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1938).

racy of the simple quadratic expression for the energy of the reaction complex. Van Vleck[9] has shown that the electron pairing formula for CH_4 gives a very good approximation to the energy and the same condition should be true of the above quadratic expression. However, if such a proposition were proved to be true, it would be of general importance inasmuch as it would become possible in general to treat reactions involving hydrogen atoms or molecules with hydrocarbons in terms of a simple quadratic expression for the energy.

The spin theory shows that the doublet energies for a nine-electron problem are expressible in terms of a forty-two-row determinant. The forty-two linearly independent bond functions can be broken up into the six rotation groups given below.

$$\left.\begin{matrix}\psi_1=a\text{–}j\ b\text{–}i\ c\text{–}h\ d\text{–}g\ e\text{–}f\\ \vdots \qquad\qquad \vdots\\ \psi_5\end{matrix}\right\} \quad \text{I}$$

$$\left.\begin{matrix}\psi_6=a\text{–}j\ b\text{–}c\ d\text{–}e\ f\text{–}g\ h\text{–}i\\ \psi_7\end{matrix}\right\} \quad \text{II}$$

$$\left.\begin{matrix}\psi_8=a\text{–}j\ b\text{–}i\ c\text{–}d\ e\text{–}f\ g\text{–}h\\ \vdots \qquad\qquad \vdots\\ \psi_{17}\end{matrix}\right\} \quad \text{III}$$

$$\left.\begin{matrix}\psi_{18}=a\text{–}j\ b\text{–}i\ c\text{–}h\ d\text{–}e\ f\text{–}g\\ \vdots \qquad\qquad \vdots\\ \psi_{27}\end{matrix}\right\} \quad \text{IV}$$

$$\left.\begin{matrix}\psi_{28}=a\text{–}h\ b\text{–}c\ d\text{–}g\ e\text{–}f\ i\text{–}j\\ \vdots \qquad\qquad \vdots\\ \psi_{37}\end{matrix}\right\} \quad \text{V}$$

$$\left.\begin{matrix}\psi_{38}=a\text{–}b\ c\text{–}h\ d\text{–}e\ f\text{–}g\ i\text{–}j\\ \vdots \qquad\qquad \vdots\\ \psi_{42}\end{matrix}\right\} \quad \text{VI}$$

The other members of a group are obtained by applying the cyclic permutation (*abcdefghij*) to the preceding member.

The group of trigonal symmetry C_{3v} has six elements and three classes, the identity E constituting a class by itself, C_1; the elements A, B and C corresponding to the operations (*eg*) (*fh*), (*cg*) (*dh*) and (*ce*) (*df*) belong to the class C_2, while the elements D and F corresponding to the operations (*cge*) (*dhf*) and (*ceg*) (*dfh*) belong to the third class C_3. The characters of the classes C_1, C_2 and C_3 for the identical representation are 1,1 and 2, respectively. Using the group theoretic relationship $1/N\sum_i h_i\chi_i'\chi_i=n$ where $N=6$ is the number of members of the group, h_i is the number of members of the class i, χ_i' is the character of the ith class for the reducible representation and χ_i is the character of the ith class of the irreducible representation we calculate the number of identical representations n to be 11. Thus the original 42-row determinant is reduced to an eleven-row determinant. For the symmetrical complex $H-CH_3-H$ there is introduced an extra plane of symmetry with the result that the number of elements of the group is doubled and n is reduced to 7. The seven-row determinant for symmetrical CH_5 was not calculated.* The eleven eigenfunctions are given in Table III. The matrix elements for the eleven-row determinant are not given because of the great amount of space required but may be obtained by any one who might require them by communicating with this laboratory.

The matrix components were calculated according to the rules formulated by Eyring and Kimball.[10]

We have calculated the energy of the lowest state for the configuration $r_1=r_2=1.12$A, $\omega=90°$, by solving the 11-row determinant. The energy thus calculated is approximately 2 kcal. lower than that given by Eq. (5). Since this additional resonance will be smaller for the configurations involved in the activated complexes of the above reactions, we conclude that the quadratic form for the energy is adequate in this type of reaction.

TABLE III.

$$\Psi_1=\psi_7$$
$$\Psi_2=\psi_8$$
$$\Psi_3=\psi_1+\psi_{29}+\psi_{38}$$
$$\Psi_4=\psi_{16}+\psi_{19}+\psi_{25}$$
$$\Psi_5=\psi_{12}+\psi_{14}+\psi_{23}$$
$$\Psi_6=\psi_{10}+\psi_{21}+\psi_{27}$$
$$\Psi_7=\psi_{36}+\psi_{39}+\psi_{42}$$
$$\Psi_8=\psi_6+A\psi_6+B\psi_6+C\psi_6+D\psi_6+F\psi_6$$
$$\Psi_9=\psi_5+\psi_{35}+A\psi_5$$
$$\Psi_{10}=\psi_4+\psi_{31}+\psi_3+A\psi_4+B\psi_4+F\psi_4$$
$$\Psi_{11}=\psi_2+\psi_{37}+C\psi_2$$

[9] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

* For more details on these group theoretic considerations, see H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933).

[10] H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 626 (1933); see also L. Pauling, J. Chem. Phys. **1**, 280 (1933).

Walden Inversion Reactions

It has been observed that iodine atoms both in solution and in the gas phase are capable of racemizing the optically active compounds $R_1R_2R_3CI$. Iodine ions also racemize these optically active compounds. The observed activation energy[11] of these processes is of the order of 14–18 kcal. These observations have been interpreted as indicating an inversion reaction similar to reaction (1). However, reaction (2) would also lead to racemization in the gas phase since the radical $CR_1R_2R_3$ is either flat or so nearly so that it is, practically, as apt to form one optical isomer as another on reforming the iodide. Free radicals react very readily with iodine vapor so that the activation energy of the reaction $CR_3+I_2\rightarrow CR_3I+I$ is probably less than 5 kcal. The heat of the reaction is about 10 kcal. since the strength of the C−I bond is about 10 kcal. greater than that of the I−I bond. The heat of activation of the reaction $CR_3I+I\rightarrow CR_3+I_2$ should then be of the order of 15 kcal. which is just that observed.

On the other hand, the inversion reaction corresponding to reaction (1) should take place much more easily in this case. The activation energy of 37 kcal. for reaction (1) arises almost entirely from the work necessary to push three of the hydrogen atoms into a plane. For free methyl, on the other hand, the flat configuration is the stable one and hence it is to be expected that the weaker the bond between the alkyl radical and the inverting atom the easier it would be to push the three groups into the plane and therefore for inversion to take place. Accordingly we would expect that it would take approximately $37\times 40/100 = 15$ cal. to invert the iodide, where 40/100 is the ratio of the strength of the C−I to C−H bonds. On this basis, then, we would expect that the inversion reaction in this case would also occur.

Rice and Teller[4] have calculated the energy required to invert methane from the frequency ${}^3\delta = 1304$ cm^{-1} corresponding to three of the hydrogen atoms moving into the plane of the carbon, upon the assumption that the restoring forces are harmonic all the way into the plane. Surprisingly enough the frequency of the corresponding vibration of CH_3I, $\delta_i||$, is only slightly less; namely, 1252 cm^{-1}. The high frequency probably arises to a considerable extent from repulsions between the iodine and the hydrogens rather than from valence bending as in methane. Now we can say the activation energy must be less than the 40 cal. required to dissociate the C−I bond. We can picture the reaction, then, as occurring in the following way: the C−I bond is stretched, allowing the three substituents to go into the plane more easily at the same time. This stretching of the C−I bond increases the attraction for an iodine atom coming up from the other side, which will in turn repel the three substituents and make it still easier for them to go into the plane. At any rate we can say that an activation energy for this reaction must be considerably less than 40 kcal. and probably not more than 20 kcal. A similar argument has been proposed by Rice and Teller.[11a]

Reactions of Hydrogen and Deuterium Atoms with Ethane and Higher Hydrocarbons. Atomic Cracking Reactions

Trenner, Morikawa and Taylor[7] found that the main products in the reaction of deuterium atoms with ethane were large quantities of deuterium-substituted methanes. This was interpreted as indicating a reaction

$$D+CH_3-CH_3\rightarrow CH_3D+CH_3, \qquad (1)$$

analogous to the inversion type of reaction as discussed above in the case of methane. Steacie[12] has also confirmed the formation of large quantities of methane in the reaction of hydrogen atoms with ethane and agrees with the mechanism proposed by Trenner, Morikawa and Taylor. In analogy with the corresponding reaction with methane and in agreement with Rice and Teller this reaction can now be ruled out since, in accordance with our calculations, it should have an activation energy of around 30 kcal. as compared with the observed activation energy of 7.2 kcal.

We give an alternative mechanism based on the reaction

$$C_2H_5+H\rightarrow 2CH_3$$

[11] E. Bergmann, M. Polanyi and A. Szabó, Zeits. f. physik. Chemie **20B**, 161 (1933); R. A. Ogg and M. Polanyi, Trans. Faraday Soc. **31**, 482 (1935).

[11a] F. O. Rice and E. Teller, J. Chem. Phys. **7**, 199 (1939).

[12] E. W. R. Steacie, J. Chem. Phys. **6**, 38 (1938).

which fits the experimental results better than one based on the inversion reaction (1). In a recent publication this mechanism has been considered as an alternative possibility by Taylor.[13]

$$C_2H_6+D\rightarrow C_2H_5+HD, \quad (2)$$

$$C_2H_5+D\rightarrow CH_3+CH_2D, \quad (3a)$$

$$CH_3+D+M\rightarrow CH_3D+M, \quad (4)$$

$$CH_2D+D+M\rightarrow CH_2D_2+M, \quad (5)$$

$$M+CH_2D+CH_3\rightarrow C_2H_5D+M, \text{ etc.} \quad (6)$$

The formation of methane comes about, therefore, as a result of reaction (3a). Reactions (2) and (3a) together we call the atomic cracking reactions. Trenner, Morikawa and Taylor have considered the possibility of atomic cracking reactions such as (3) but decided against them since they considered them inconsistent with the results of Taylor and Hill[14] on the hydrogenation of ethylenes. We do not, however, see anything in these latter results which contradicts the mechanism here put forth. When a deuterium or hydrogen atom approaches an ethyl radical an excited ethane molecule is formed with an amount of excitation energy equal to the strength of the C−H bond. This energy does not remain localized in the C−H bond but is redistributed among the vibrational degrees of freedom until sufficient energy becomes localized in the C−C bond to split it or else in the C−D bond to redissociate it. Even if the C_2H_5D complex suffers a collision before it dissociates it will not lead to stabilization as an ethane molecule, since it can lose ten or more calories and still have enough energy to break the C−C bond. We therefore expect that no deuterized ethane can be formed by the recombination of C_2H_5 and D except perhaps at high pressures, but that it will preferably split into two methyl radicals. The methyl radicals can then either combine with deuterium atoms to give CH_3D and CH_2D_2 or, having lost their excess energy, recombine to give C_2H_5D. The higher the concentration of deuterium atoms the less probable would be recombination to give substituted ethanes. It is not surprising therefore that in a few of the experiments of Trenner, Morikawa, and Taylor where a high relative concentration of D atoms was obtained no substitution was found in the ethane although highly deuterized methane was formed. The lowest amount of deuterization of the methane formed was found to be 35 percent, while we see that the above sequence of reactions gives $37\frac{1}{2}$ percent. Thus we must consider that the reaction $CH_3+C_2H_6\rightarrow C_2H_5+CH_4$ does not occur under these circumstances, since it would reduce the percentage of deuterization below 35 percent.

Up to 63 percent deuterization of the methane is observed, however, so that in addition we must consider deuterization reactions such as

$$C_2H_5+D\rightarrow C_2H_5D'\rightarrow C_2H_4D+H, \quad (7)$$

$$C_2H_5+D\rightarrow C_2H_4+HD, \quad (8)$$

$$M+C_2H_4+D\rightarrow M+C_2H_4D, \quad (9)$$

followed by

$$C_2H_4D+D\rightarrow CH_2D+CH_2D. \quad (3b)$$

Reaction (7) is analogous to (3a); (3a) should be more probable, however, since the C−C bond is weaker and the chance of sufficient energy accumulating there to break the C−C bond is correspondingly greater. Reaction (8) would no doubt involve a small activation energy. If the one D atom went in by reaction (7) or by (8) and (9) before (3b) occurred, then one would expect the methane to be 50 percent exchanged; if on the average two hydrogens were exchanged with deuterium atoms in the ethyl radical before (3b) took place, the methane would be $62\frac{1}{2}$ percent exchanged. As a matter of fact, the observed figures in the different experiments of Trenner, Morikawa and Taylor correspond to 35 percent, 50 percent and 63 percent deuterization of the methane.

Trenner, Morikawa and Taylor suggest that the high deuterium content of the methane is to be explained by rapid exchange of the methyl radicals by such reactions as,—

$$CH_3+D\rightarrow CH_3D'\rightarrow CH_2D+H \quad (10)$$

or

$$CH_3+D\rightarrow CH_2+HD \quad (11)$$

followed by

$$CH_2+D+M\rightarrow CH_2D+M,$$
$$CH_2D+D+M\rightarrow CH_2D_2+M.$$

[13] H. S. Taylor, J. Phys. Chem. **42**, 763 (1938).
[14] H. S. Taylor and D. Hill, J. Am. Chem. Soc. **51**, 2922 (1929).

Reaction (10) is not very probable since the deuterium atom approaches along an axis of symmetry and consequently when the energy is redistributed the three hydrogen atoms must move out symmetrically and the energy could not become concentrated in a single C−H bond. Reaction (11) cannot be ruled out and it is difficult to say at present whether the deuterization occurs by the sequence (7), (8) or (9) or by reactions of the type (11).

The reactions of deuterium with propane and butane were found by Trenner, Morikawa, and Taylor to be somewhat slower than the corresponding reaction with ethane. Due to the increased complexity of the radicals C_3H_7 and C_4H_9 as compared with the C_2H_5 radicals it becomes increasingly more difficult for the energy of the quasi-molecule RD* to become localized in any one C−C bond and so we might expect some stabilization of the C_3H_7D and C_4H_9D radicals to give the stable propane and butane molecules, respectively. The very low deuterium content of the residual propane argues against this process being very frequent.

In the case of propane much more methane was formed than ethane while from butane considerably more methane was formed than either ethane or propane. This result is readily explained by reactions of the atomic cracking type. Thus in the case of butane we would have the following reactions

$$C_4H_{10}+D\rightarrow C_4H_9+HD$$

followed by

$$C_4H_9+D\rightarrow C_4H_9D'\begin{cases}\nearrow CH_2D+C_3H_7\\ \searrow C_2H_5+C_2H_4D.\end{cases}$$

The propyl radical would then be cracked further to CH_3 or C_2H_5 by another D atom or could be stabilized by a third body to give propane. The ethyl radicals will also be cracked further resulting in an excess of methane in the products.

This interpretation of the results of Trenner, Morikawa and Taylor leads to the assignment of their activation energy of 7.2 kcal. to the reaction

$$D+C_2H_6\rightarrow C_2H_5+HD$$

rather than to the reaction $D+C_2H_6\rightarrow CH_3D+\dot{C}H_3$. This is to be compared with the value 6.4 kcal. found by Steacie and Phillips[5] for the same reaction.

Experimental Evidence for the Existence of the CH_3-H-H Complex

Farkas and Melville[15] have carried out some very interesting experiments on the rate of the *ortho-para* conversion and the rate of exchange of hydrogen and deuterium in the presence of water, ammonia and methane. While the presence of water and ammonia caused only a slight decrease in the rate of conversion of ortho- to parahydrogen induced by excited mercury atoms, methane above 150°C slowed down the rate of conversion very markedly. Thus at 238°C the rate of conversion is eight times slower in the presence than in the absence of methane. This indicates that methane removes hydrogen atoms from the system and indeed in the above-mentioned experiment the methane reduces the concentration of hydrogen atoms eightfold. These experiments can be interpreted in terms of the intermediate complex CH_3-H-H theoretically postulated. The catalytic effect of methane in causing the recombination of hydrogen atoms can then be interpreted in terms of the reactions:

$$M+H+CH_4\rightarrow CH_3-H-H+M$$
$$CH_3-H-H+H\rightarrow CH_4+H_2$$
or $$CH_3-H-H+H-H-CH_3\rightarrow H_2+2CH_4.$$

Our quantum-mechanical calculations have led us to the conclusion that before a hydrogen atom can be adsorbed on methane it must go over a potential barrier 10 kcal. in height. This is in agreement with the data of Farkas and Melville, since they find that the catalytic efficiency of methane for the recombination of hydrogen atoms rises rapidly with the temperature, reaches a maximum and then decreases beyond 280°C. The decrease at high temperatures is explained, since because of the weak nature of the Coulomb bond between a hydrogen atom and methane, the equilibrium would be in favor of the dissociated state at moderately high temperatures.

It should be remarked that according to our calculations the potential barrier for the formation of CH_3-H-H is the same as for the reac-

[15] A. Farkas and H. W. Melville, Proc. Roy. Soc. **A157**, 625 (1936).

tion $H+CH_4 \rightarrow CH_3+H_2$. It is therefore to be expected that unless the CH_3-H-H complex is stabilized by a collision this reaction will take place. If the reaction were carried out in the presence of deuterium there would thus be a competition between the exchange reaction and the catalytic recombination of the deuterium atoms, the ratio of the rates of the two reactions depending upon the pressure. Thus the quantum efficiency of 0.1 at 189°C and 100 mm pressure indicates that the chance of a CH_4D being stabilized before decomposing into CH_3 and HD is 9/10. As the temperature is raised the CH_4D complex will tend more and more to be in equilibrium with respect to dissociation into CH_4+D and the rate of disappearance of deuterium atoms will depend upon the rate of the reaction $D+CH_4D \rightarrow CH_4+D_2$ and consequently at high temperatures the rate of the *ortho-para* conversion will depend on the square root of the light intensity as is observed. At the same time, of course, the quantum efficiency of the methane reaction will rise with rising temperature. According to this interpretation the hydrogen atom concentration should become proportional to the first power of the light intensity at intermediate temperatures. At still lower temperatures the hydrogen atoms will disappear by the reaction $H+H+M \rightarrow H_2+M$ and the hydrogen atom concentration will again be proportional to the square root of the light intensity. It should be mentioned that Farkas[16] has put forth a similar hypothesis to explain the low hydrogen atom concentration found in the photochemical ammonia decomposition; namely, the formation of an NH_4 molecule with a stability of 10 kcal. with respect to decomposition into ammonia and a hydrogen atom. Taylor and Jungers[17] have shown that in such an NH_4 complex the four hydrogens are not equivalent since no exchange reaction takes place with ammonia in the presence of deuterium atoms. The same type of calculations which showed H_3C-H-H to be stable would no doubt show H_2N-H-H to be the stable complex in this case also. The existence of Coulomb bonds in reactions involving free radicals is no doubt a general one and probably plays a big role in these reactions. This feature of radical reactions has generally been neglected in the past and this neglect has lead to the confusing of observed energies of activation for adsorbed atoms or radicals with the lower value for the free atoms. Thus, a Coulomb bond between chlorine atoms and chlorine was indicated by quantum mechanical calculations of Rollefson and Eyring.[18] Craggs, Squire and Allmand[19] find it necessary to introduce the Cl_3 molecule to explain their results on the photochemical hydrogen chlorine reaction. However, in this case the evidence is inconclusive.

[16] L. Farkas and P. Harteck, Zeits. f. physik. Chemie **B25**, 257 (1937).
[17] H. S. Taylor and J. C. Jungers, J. Chem. Phys. **2**, 452 (1934).

The Absolute Rate of the Unimolecular Decomposition of Ethane and the Recombination of Free Radicals

An expression for the absolute rate of the recombination of free radicals was given by one of us.[20]

$$k=\frac{3\pi}{2}\left(\frac{kT}{2}\right)^{1/6}\frac{1}{\sigma_{AB}}\left(\frac{\alpha_A\alpha_B I_A I_B}{I_A+I_B}\right)^{1/3} \times\frac{M_A M_B}{(M_A+M_B)^{5/2}}\kappa. \quad (6)$$

This expression was derived upon the assumption that in this case there is no activation energy in the true sense of the word. The radicals attract each other at large distances largely by means of polarization forces. This attractive force is opposed by the centrifugal force of the rotation of the two radicals considered as a diatomic rotator. The superposition of these two forces gives rise to a slight potential barrier, the top of which corresponds to the activated complex. In addition it was assumed that, at the activated state, the two radicals were so far apart that their rotational and vibrational degrees of freedom were the same as for the isolated free radicals.

In this expression σ_{AB} is the symmetry number

[18] G. K. Rollefson and H. Eyring, J. Am. Chem. Soc. **54**, 170 (1932).
[19] Craggs, Squire and Allmand, J. Chem. Soc., 1878 (1937).
[20] E. Gorin, Acta Physicochemica U. R. S. S. **9**, 681 (1938).

of the two free radicals considered as a diatomic rotator, i.e., $\sigma_{AB}=1$ for $A\neq B$ and $\sigma_{AB}=2$ for $A=B$. α_A, α_B, I_A, I_B, M_A, M_B are the polarizibilities, ionization potentials, and masses of the radicals A and B, respectively, and κ is the transmission coefficient. For a bound methyl radical the value 2.25×10^{-24} cc is given[21] for the polarizibility. This will no doubt be somewhat higher for the free radical since the odd electron is more easily polarizible in the free radical. We have accordingly used the value 2.5×10^{-24} cc for α. We have used Mulliken's[22] value for the ionization potential of the methyl radical, namely, 8.4 volts. The insertion of these values in Eq. (6) gives for the rate of recombination of two methyl radicals at 873°K 2.54×10^{-11} cc/mole/sec. If κ is set equal to unity this gives a maximum value for the rate of 2.54×10^{-11}. This is a maximum since we have assumed that the radicals rotate freely in the activated state. However their rotational degrees of freedom other than that around the symmetry axis must be considered as being in the nature of a weak vibration. This may cause the rate to be lowered by a factor of about two or three. In addition a value of κ somewhat less than unity is not improbable. This gives the rate at high pressures. At moderately low pressures, redissociation before stabilization becomes frequent.

Rice and Herzfeld[23] usually assign a value of 8000 cal. to the activation energy in the recombination of free radicals. It is therefore necessary to examine our assumption of zero activation energy for the recombination of two methyl radicals a little more closely. It might be thought at first sight that the fact that free methyl radicals are flat while in ethane they are tetrahedral would give rise to an activation energy arising from the transition from flat to tetrahedral models. On closer examination we see that this is not so, however, since the attraction between the two free carbon orbitals, in even flat methyl, more than overbalances at large distances one-half the sum of the hydrogen repulsions. This is so because the carbon-carbon interactions act over a much longer range than the hydrogen-hydrogen interactions. This can be seen at least qualitatively from a comparison of a H−H with a C−C Morse curve. The flat radicals thus attract one another at large distances and as they approach the attached hydrogens slip over without activation energy to the positions they occupy in normal ethane. It should be pointed out that free radicals as well as hydrogen atoms are capable of forming Coulomb bonds with hydrocarbon molecules. Activation energies for reactions involving the adsorbed free radicals would no doubt be higher than would otherwise be expected and an activation energy of 8 kcal. for their recombination as postulated by Rice and Herzfeld is not unreasonable.

In order to calculate the absolute rate of the decomposition of ethane into two methyl radicals it is necessary to know the equilibrium constant K for this reaction. The absolute rate of decomposition is then given by $k_f=k_bK$ where k_b is the rate of recombination calculated above. K is given by the expression

$$K=\frac{k_f}{k_b}=\frac{(CH_3)^2}{C_2H_6}=\frac{(F_{CH_3})^2}{F_{C_2H_6}}e^{-\Delta E_0/RT},$$

where F_{CH_3} is the partition function for the methyl radical and $F_{C_2H_6}$ the partition function of the ethane molecule. ΔE_0 is the heat of the reaction at absolute zero and

$$F_{CH_3}=F_{trans}F_{vib}F_{rot}$$

while for ethane we have in addition the partition function for internal rotation, i.e.,

$$F_{C_2H_6}=F_{trans}F_{vib}F_{rot}F_{int\ rot}.$$

The vibrational part of the partition function F_{vib} is given by

$$\Pi_i\frac{1}{1-e^{-h\nu i/kT}}.$$

For the methyl radical the internal frequencies of the methyl group in CH_3I were chosen: $\delta_i\|=1252$ cm^{-1}, $\nu_i^2\|=2860$, $^2\delta\perp^2=1445$, $^2\nu\perp=3074$, the last two frequencies being doubly degenerate.[24] Howard's[25] assignment of frequencies was used

[21] Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, p. 985.
[22] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).
[23] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[24] H. Sponer, *Molekulspectren* (Julius Springer, 1935).
[25] J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

for ethane; namely, 993 cm^{-1}, 1460, 2927, 1380, 2960, and 827, 1480, 3000, 1005, 1515, 3025, where the last six frequencies are doubly degenerate. For the rotational partition function for ethane and methyl we use that of a symmetrical top:

$$F_{\text{rot}}=\frac{8\pi^2(8\pi^3 I_z^2 I_x)^{\frac{1}{2}}}{\sigma h^3}.$$

For ethane σ, the symmetry number, is 18 while the values $I_z=40.1\times10^{-40}$, $I_x=10.8\times10^{-40}$ were taken from Kemp and Pitzer.[26] For the methyl radical $\sigma=6$ since it is flat and $I_z=I_{x/2}=6.30\times10^{-40}$ is the value calculated on the basis of a C−H distance of 1.12A. In addition it is necessary to compute the partition function for internal rotation in ethane. This can be done with sufficient accuracy as follows. The potential barrier is of the form $V=\frac{1}{2}V_0(1-\cos 3\chi)$ and V_0 the height of the barrier is equal to 3000 cal. The energy levels less than V_0 in height can be roughly assigned on the assumption that the levels are those of a harmonic oscillator whose force constant is obtained from the curvature of the potential function in the neighborhood of the potential minimum. This gives a frequency of 306 cm^{-1}. We have assumed that for states lying higher than 3000 cal. we can use the ordinary partition function for a one-dimensional rotator. The total partition function is then given by

$$F_{\text{int rot}}=e^{-2560/RT}\frac{(2\pi IkT)^{\frac{1}{2}}2\pi}{h}+3(1+e^{-h\nu/kT}+e^{-2h\nu/kT}+e^{-2560/RT}).$$

The $e^{-2560/RT}$ arises from the fact that due to the zero-point energy the top of the barrier is 2560 cal. above the lowest level. The factor of three in front of the vibrational part arises from the threefold degeneracy of the vibrational levels. I is the reduced moment of inertia of the rotator and is equal to $I_{x/2}=5.4\times10^{-40}$ g/cm^2.

We thus obtain for the equilibrium constant the value $K=2.50\times10^{-25}\ e^{-\Delta E_0/RT}$ molecule/cc, and for the rate constant of the decomposition reaction the value $k_f=6.35\times10^{14}\ e^{-\Delta E_0/RT}$. As discussed above k_f may be reduced by a factor of two or three by considering the restriction of free rotation of the methyl groups in the activated state. The simplified formula $k=\nu e^{-E/RT}$ where ν is the frequency of the C−C vibration would give as is expected a smaller value for the preexponential factor; namely, 4×10^{13}. The value of 10^{14} given by Rice and Herzfeld is thus of the right order of magnitude and is probably correct within a factor of three.

We wish to express our appreciation to Professors H. S. Taylor and R. N. Pease for helpful discussions.

[26] J. D. Kemp and K. S. Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).

Discussion

H. Austin Taylor, *New York University:* I should like to ask Professor Eyring whether he examined in detail the potential energy surface corresponding to the reaction CH_3+H_2. Fig. 9 in the text goes only as far as 1.6 angstroms for the C−H distance. Since the reaction $H+H_2$ requires an energy of activation it is not unreasonable to expect one for CH_3+H_2. Might this not be outside the range covered by Fig. 9? Again, the argument for the absence of an energy of activation for the combination of two methyl radicals is based on the fact that the carbon-carbon interactions seen from a C−C Morse curve, act over a much longer range than the H−H interactions. I should like to ask if this C−C Morse curve is for divalent carbon and whether the situation might not conceivably be different for the interactions of the carbons in two methyl groups.

Henry Eyring, *Princeton University:* The surface for the reaction $H+CH_4\rightarrow H-H-CH_3\rightarrow H_2+CH_3$ was explored sufficiently beyond the C−H distance to ascertain that there was no other energy barrier along the reaction path as high as the one encountered at the H−H distance of 1.4A (see Fig. 9). A lower barrier probably exists but its height was not of especial interest in our considerations. The C−C Morse curves used in estimating the activation energy for the recombination of two methyl radicals was for the single C−C bond in hydrocarbons. The uncer-

tainties in $r=1.54$A, $\omega=990$ cm^{-1}, $D=80$ kcal. seem unlikely to affect our qualitative conclusion that there is no activation energy. Our method of estimation of this quantity is necessarily rough.

K. F. Bonhoeffer, *University of Leipzig:* I conclude that you regard methane as an efficient catalyst for the combination of hydrogen atoms but there is no such effect observed with a hydrogen discharge tube in which the hydrogen atoms have long lives. May there not be other factors involved?

Henry Eyring, *Princeton University:* Both the results of Melville and Farkas and our theory require that methane should not catalyze the recombination of hydrogen atoms at room temperature. This is also in accordance with Professor Bonhoeffer's findings. The lack of a room-temperature catalytic effect is a result of the activation energy associated with forming H_3CH-H. The catalytic effect becomes marked around 238°C and according to our theory should disappear again at higher temperatures because of the dissociation of H_3CH-H.

R. A. Ogg, Jr., *Stanford University:* I wish to ask if I am correct in detecting a logical error regarding the authors' proposed effect of "adsorption" of free atoms and radicals by other molecules. In the case of hydrogen atoms, the Coulomb complex with methane molecules is supposed to catalyze recombination. In the case of methyl radicals, similar complex formation is supposed by Professor Eyring to *hinder* recombination. This appears to be an inconsistency.

Further, as to methyl radicals, the remarkable experiments of Paneth and co-workers point to a very slow recombination (in fact, no positive evidence of a gas phase recombination was found) even when helium was used as a carrier gas. It seems improbable that this inertia of methyl radicals could be attributed to "adsorption" by helium atoms.

Henry Eyring, *Princeton University:* Whether an association reaction is hastened or hindered by a radical first associating with a nonreactive molecule depends on whether the advantage of dispensing with a third body compensates or does not compensate for the added activation energy. Since recombining CH_3 radicals stay together longer in the absence of a third body (to carry off the extra energy) than do H atoms, a preliminary association will be less helpful in the former case. The problem of the advantage or disadvantage of this preassociation with a saturated molecule thus becomes a quantitative one for each particular case.

Our considerations, so far, enable us to say nothing quantitative about the efficacy of helium in the recombination of CH_3 radicals.

O. K. Rice, *University of North Carolina:* It has been suggested that attachment of methyl radicals to other molecules will result in an apparent increase in the energy of activation for methyl radicals. However, I believe the effect will be the opposite, for the heat of combination will give a negative contribution to the apparent energy of activation. The energy of activation under such circumstances might even appear to be negative.

P. A. Leighton, *Stanford University:* It would appear to me that the reaction $H+CH_4\rightarrow H_2+CH_3$ is sufficient to account for the reduction in atomic hydrogen concentration by methane, observed by Farkas and Melville. At the temperature of their experiments this reaction should be quite rapid, and particularly if, as Dr. Burton concludes in his paper, the reverse reaction has the higher activation energy, it should effectively reduce the stationary concentration of hydrogen atoms.

Some Remarks on the Theory of Reaction Rates*

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Effects connected with a more complicated nature of the energy surfaces of relatively simple reactions are discussed. The theory of elementary association reactions is examined and it is shown that better results are obtained in the rate of association of atoms when three additional attraction states are taken into consideration. The rates of association of iodine, bromine and chlorine atoms are calculated and compared with the experimental rates. The improvement to be expected from consideration of the angular momentum of the associating pair of atoms is discussed.

EVERY modern theory of reaction rates has to deal with two essentially different kinds of problems. The first problem concerns the forces acting between the atoms participating in the reaction, the second one is a statistical question and aims at a calculation of the rate constant, assuming that the answer to the first question is known. We shall discuss first the reactions with, then those without, activation energy from this point of view.

I

The solution of the statistical problem is probably known at present,[1] for gas reactions with an activation energy, to such an extent that not very much further progress can be expected in this connection in the near future. To be sure, several points of the theory still remain to be cleared up,[2] particularly when quantum effects play a major role and also very few examples of nonadiabatic reactions have been considered so far in detail. However, the remaining questions are of a more special nature and appear to be so difficult that we must feel satisfied, for the time being, with a partial solution.

On the other hand, our knowledge of the forces between atoms is far from being complete enough to allow the accurate calculation of reaction rates with activation energies. Considering the difficulties involved in explaining the binding energies of well-known ordinary compounds, one will be hardly surprised to find that—apart from one single instance[3]—no accurate calculation of activation energies exists. It is more unsatisfactory that even the general character of the forces between the atoms of a reaction are known only in the very simplest cases. Although one could numerically predict rates of reactions with activation energy only if one were able to calculate the activation energy accurately, the knowledge of the general properties of the forces between atoms would be valuable in any case by enabling us to compare rates of different reactions on a more satisfactory basis.

The general character of the forces between atoms, i.e., the "energy surface," is well known only for a system of three atoms, at most, all of which are in S states. There are several reasons to believe that the energy surfaces are much more complicated in other cases than these known energy surfaces are. Firstly, the number of ways atoms in P and higher states can be orientated with respect to each other is much greater than for atoms in S states. Second, it appears at present most probable that the reason for the discrepancies between experimental and theoretical reaction rates is due to the unexpectedly complicated shape of these potential surfaces. Strong indications in the same direction are given also by preliminary calculations of Magee[4] who considered a system formed by a P and two S atoms. Finally Knipp[5] has shown that complications can arise even in the case of two atoms inasmuch as states which are known not to be attractive at short distances become weakly

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] Cf. various papers in the Trans. Faraday Soc. (1937) in the general discussion on reaction kinetics.

[2] Cf. also J. O. Hirschfelder and E. Wigner, J. Chem. Phys. (in publication).

[3] Hirschfelder, Eyring and Topley, J. Chem. Phys. 4, 170 (1936).

[4] J. L. Magee, unpublished.

[5] J. Knipp, Phys. Rev. **53**, 734 (1938).

attractive for larger separations, while states which are attractive at short distances are in many instances repulsive at large distances. Thus, there is no energy surface, as in the case of only S atoms, which is lower than all other energy surfaces for all configurations.

Possibly, the explanation of a very puzzling phenomenon, observed by Polanyi[6] and collaborators, and first emphasized in this connection by Goodeve,[7] lies also in a similar direction. The phenomenon is the excitation of a Na atom, with a probability approaching 1, by an excited NaCl* molecule obtained by the reaction $Na_2+Cl=Na+NaCl^*$. Since the whole system is, originally, on the lowest energy surface, it should remain there, according to the theory of the adiabatic nature of these reactions.[8] However, a system containing an excited Na atom is clearly not on the lowest energy surface. According to the customary ideas, the NaCl* molecule has only vibrational and rotational but no electronic excitation. The two ions in the molecule vibrate against each other very strongly—in the rather improbable case that the NaCl* contains all the reaction energy of 3.35 electron volts, the maximum distance of the Na and Cl ions becomes about 6.5A. This is, nevertheless, much less than the distance at which the molecular curve, corresponding to the ordinary heteropolar molecule, crosses[9] the molecular curve corresponding to the homopolar NaCl. This latter distance is more than 10A. Thus, for the energies available, the lowest curve is well separated from even the next curve. In the presence of an additional Na atom, i.e., during the collision of the NaCl* with Na, both molecular curves will be deformed and an overcrossing cannot be altogether excluded. However, even if such an overcrossing should occur, it hardly would lead with an appreciable probability to transitions to such highly excited energy surfaces which correspond to an excited Na atom.

It appears, on the whole, more probable that the original reaction $Na_2+Cl=Na+NaCl^*$ leads to the homopolar state of the NaCl molecule rather than the normal state. The distance at which the Na_2+Cl curve crosses the $Na_2^++Cl^-$ curve is greater than 6.7A so that there remains a large probability for a nonadiabatic behavior, i.e., for the transition to the higher, homopolar level. If this is true, the energy in NaCl is stored up to a great extent as electronic energy and it is well known that this can serve more readily than vibrational energy can, to the excitation of the electron in another atom. The weakest point of this explanation consists in the apparent absence of a reasonably deep minimum in the molecular curve of NaCl in the homopolar state. However, the evidence is not conclusive on this point.

This example should only emphasize the fact that complications can exist even in the energy surfaces of very simple systems and that these can lead to rather unexpected results. On the whole, the status of the theory of reaction rates with activation energy is that the statistical part of the theory is well developed, but our knowledge of the forces between atoms is adequate only in a few cases.

II

The status of the theory of reactions without an activation energy is rather the opposite. The statistical part of the theory offers considerable difficulties, but the details of the behavior of the forces between atoms enter in a much less critical way than for reactions with activation energy. Nevertheless, the example to follow shows that they may form, even in this case, the most important link of missing information.

Perhaps the most simple among the reactions without activation energy are those leading to a recombination of atoms by collision with a third atom and I attempted, some time ago, to derive a formula for the rate of these reactions[10] and applied it to the rate of the reaction $I+I+X=I_2+X$ which has been measured by Rabinowitch and Wood.[11]

The general idea of the calculation is illustrated in the schematic Fig. 1. In this, r is the distance of the two I atoms, p_r the corresponding momentum, x a coordinate of the third body X,

[6] H. Beutler and M. Polanyi, Zeits. f. Physik **47**, 379 (1928); Zeits. f. physik. Chemie **1B**, 3 (1928); St. v. Bogdandy and M. Polanyi, *ibid.* **1B**, 21 (1928); M. Polanyi and G. Schay, *ibid.* **1B**, 30 (1938).

[7] C. F. Goodeve, Trans. Faraday Soc. **30**, 60 (1934).

[8] F. London, *Sommerfeld Festschrift* (Leipzig, 1928), p. 104.

[9] F. London, Zeits. f. Physik **74**, 143 (1932).

[10] E. Wigner, J. Chem. Phys. **5**, 720 (1937).

[11] E. Rabinowitch and W. C. Wood, J. Chem. Phys. **4**, 497 (1936).

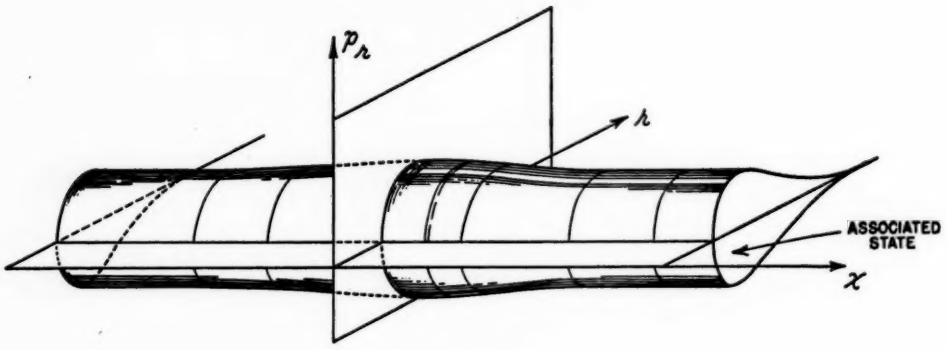

FIG. 1.

measured from the center of the two I atoms. The other 15 coordinates of the phase space are suppressed in the figure, for sake of simplicity.

The rate is defined as the number of pairs of I atoms passing in unit time from the dissociated into the associated state. For large values of x, positive or negative, there is no doubt which part of the figure corresponds to associated and which to dissociated atoms: the former is the region in which the relative energy $V(r) + \frac{1}{2}p_r^2/m_r$ of the two I atoms is negative, the latter in which it is positive. ($V(r)$ is the potential energy of the I atoms with respect to each other, m_r is their relative mass.) The region corresponding to the associated state lies within the surface shown on the figure. The paths of the different systems are lines in the phase space and the reaction rate is the number of such lines crossing the surface and entering the associated region. At large values of x, the paths in the neighborhood of the surface are parallel to it and do not cross it since the relative energy of the two I atoms is a constant of the motion if the X is far away. This is only another expression of the fact that the association can only occur in the neighborhood of the third body X, i.e., for small values of x.

There will be some paths which enter the associated region but leave it immediately afterwards—these, of course, should not be counted as associations. One will, therefore, draw the surface at small values of x in such a way that the number of paths crossing it shall be as small as possible. This condition, while not changing the shape of the surface at large values of x (where no crossings occur, anyway), will change it at small values of x. It will be such that no paths will cross it in one direction just to cross it again soon afterwards in the opposite direction; all paths crossing it will stay inside while x increases to large positive or negative values. The number of paths crossing this surface will give the real association rate, while the number of paths crossing any other surface, e.g., the surface shown on the figure, will be *greater* than the real association rate. Of course, the actual calculation must be done for the 18-dimensional phase space —not for the schematic space of the figure.

It is clear then, that the calculated rate should be greater than the observed one. Nevertheless, Table I taken from reference 10 and completed with the results of a similar calculation on Br atoms shows that this is not the case. The values are given in units of 10^{-32} (molecule/cc)$^{-2}$ sec.$^{-1}$, the different columns refer to the different "third bodies" X used for the reaction. The computation has been carried out exactly as described in reference 10. For the radius of Br, that of Kr, 1.59A was assumed.[12] The rate of measurements for Br are also due to Rabinowitch and Wood.[13]

TABLE I.

X	He	A	H_2	N_2	O_2
Br exp.	0.76	1.3	2.2	2.5	3.2
theor.	1.6	2.1	1.7	2.3	2.2
I exp.	1.8	3.8	4.0	6.6	10.5
theor.	1.5	2.1	1.8	2.3	2.2
Cl theor.	1.9	2.5	2.2	2.8	2.7

[12] Cf. *Landolt-Börnstein's Tables*, Vol. I, p. 69.
[13] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 907 (1936).

It should be remarked, however, that the earlier work of Hilferding and Steiner[13a] gave substantially lower results.

Of course, the extremely large discrepancy for H_2 and N_2 is not alarming as it is not permissible to treat these as atoms. But a discrepancy obtains for the I association in the case of He and A also, and every improvement of the calculation makes this necessarily only worse. In fact, an improvement of the calculation, to be discussed later, decreases the calculated values approximately by a factor 2.

Several possible reasons for this discrepancy have been discussed, among others the possible existence of other attractive states of the two I atoms, in addition to the one leading to the normal I_2 molecule. It now seems that this is the cause of the discrepancy.

One should remember that the system formed by two I atoms and a He atom can be in 16 different quantum states, corresponding to the four possible orientations of the angular momenta of each I atom with respect to each other and to the internuclear axis. Only one-sixteenth of all pairs of I atoms will be in any specified one of these quantum states and if only one of these states were attractive, the association could occur only for one-sixteenth of all pairs of I atoms. In this case—and this was assumed at the calculation of Table I—the association rate would be 16 times smaller than it would be for 16 equally attractive states.

E. Rabinowitch[14] has considered the interpretation of his and Wood's experiments in a very interesting fashion from the point of view of the simple collision theory. He pointed out that there are indications[15] that among the molecular curves obtained by approaching two I atoms in their normal states, there are at least four which are attractive. One of these is simple and corresponds to the normal state of I_2, the other three are doubly degenerate each but, of course, less strongly attractive than the first one, Rabinowitch concludes that no "statistical factor," corresponding to our $\frac{1}{16}$ should be taken into account for the consideration of the association rate. This is, perhaps, somewhat exaggerated, as there are certainly several repulsive states of two I atoms and these hardly can be expected to lead to a recombination. On the other hand, the rate of recombination into the three less strongly attractive states should also be calculated and added to the rate of recombination into the normal state of I_2. The values of the integrals over the three additional molecular curves of I_2 have been obtained by a graphical integration of Cordes' estimated curves. It gave 35×10^{-36} erg cm^3 for the integral $-\int V(r)r^2dr$ and 129×10^{-44} erg cm^4 for the integral of $-\int V(r)r^3dr$ for the three less strongly attractive states together. These numbers should be multiplied by two on account of the statistical weight of these states. The corresponding integrals for the normal state of I_2 are 33.5×10^{-36} erg cm^3 and 114×10^{-44} erg cm^4 if taken from Cordes' curve and 27×10^{-36} and 91×10^{-44}, respectively, if computed by Morse's formula, as outlined in reference 10. A similar calculation has been done for Br also, although on an even less secure basis. The rates calculated for the number of transitions into all four states are shown in Table II in the same units as in Table I.

TABLE II.

	He	A	H_2	N_2
I exp.	1.8	3.8	4.0	6.6
theor.	6.1	7.7	6.4	8.1
Br exp.	0.76	1.3	2.2	2.5
theor.	4.25	5.4	4.5	5.9

Considering the crudeness of the calculation and the fact that the rate could be calculated in terms of constants obtained from entirely different sources, the agreement is as good as can be expected. The relation between calculated and observed values is as it should be; the latter ones are several times smaller than the former ones. Even a larger ratio between calculated and observed values would not be disturbing as the former ones must be, by the very nature of their derivation, too large and every improvement of

[13a] Zeits. f. physik. Chemie **B30**, 399 (1935).
[14] E. Rabinowitch, Trans. Faraday Soc. **33**, 283 (1937).
[15] Cf. R. S. Mulliken, Phys. Rev. **46**, 549 (1934); W. G. Brown, *ibid.* **42**, 355 (1932); H. Cordes, Zeits. f. Physik **97**, 603 (1935). *Note added in proof.*—Professor Mulliken has kindly informed me that he does not consider the evidence leading to the second lowest curve ($^1\Pi_u$) of Cordes to be satisfactory. In fact, theoretical considerations lead him to expect this state to be repulsive. In this case, the theoretical values of Table II should be reduced by about 30 percent.

the calculation—e.g., the one to be outlined below—will bring the two values nearer to each other.

The apparently better agreement for H_2 and N_2 has no significance as the formulas apply only for atoms. It is somewhat surprising that the ratio of the calculated rates for Br and I is so much smaller than the experimental ratio.

An improvement of the calculation can be obtained on the basis of the following consideration: A molecule becomes stabilized even if its energy is greater than zero if it contains mainly rotational and only to a smaller extent vibrational energy.[16] Denoting the angular momentum by μ, a diatomic molecule is (apart from quantum-mechanical effects) stable if its total energy is smaller than $\mu^2/2m_r r_\mu^2$ and the separation of its atoms smaller than r_μ where m_r is the relative mass of the atoms in the molecule and r_μ the distance at which $V(r)+\mu^2/2m_r r^2$ assumes its maximum value. In this way, a molecule can accumulate substantially greater energy amounts than sufficient for its dissociation. This fact gives us the possibility to place the boundary dividing the free state from the associated state not at the place where the relative energy of the pair is zero, but at the place where, at a separation $r<r_\mu$, the relative energy $\frac{1}{2}m_r v_r^2+V(r)$ becomes smaller than $\mu^2/2mr_\mu^2$. *A priori*, both procedures are justified. The more useful procedure will be, however, that one which gives the smaller upper limit for the rate. Naturally, even the rate obtained with the new calculation will be only an upper limit for the actual rate, as the relative energy can rise above $\mu^2/2mr_\mu^2$ immediately after it falls below this value. The reason that the old calculation gave higher rates than the new one is that it considered the number of pairs of atoms with a positive total energy to have the equilibrium value. It has, however, a lower value in reality, since the above-described metastable states with positive energy are more quickly impoverished by collisions of the second kind than they are replenished by the processes which we are considering now. The old calculation counts as associations these collisions of the second kind also (which is correct) and assumes that the metastable molecules are present in the amount which is in equilibrium with the free atoms. It is the avoiding of this last assumption which constitutes the improvement of the calculation as outlined above.

It is clear, however, that the computation becomes much more involved and its details will not be given here. The calculated rates are reduced by almost a factor 2 and the agreement of Table II much improved.

[16] Cf. G. Herzberg, Erg. exact. Naturw. **10**, 207 (1931).

Discussion

E. P. Wigner, *Princeton University:* I wish to make some remarks concerning the adiabatic hypothesis. The adiabatic hypothesis states that the atoms can be considered to move under the influence of a potential. This means, physically, that the electronic motion adjusts itself quickly enough to the changing positions of the nuclei so that no change in the electronic excitation occurs. Clearly, if the electrons become excited, the corresponding excitation energy is unavailable for the motion of the nuclei, and these do not seem to move any more as under the influence of a steady potential.

The conditions for the validity of the adiabatic hypothesis have been investigated repeatedly from the theoretical standpoint. I wish to point to some information, obtained on the basis of experimental evidence, concerning the validity of this hypothesis.

The infraction of the adiabatic hypothesis can be visualized in the following way. Given two atoms in their normal states, there will be a potential between them. If one or both atoms are excited, the forces will be different and we have, therefore, several potential curves (or "energy surfaces" in case of more than two atoms). If we start out with a certain energy and the two atoms in their normal states, the excess energy is present as the kinetic energy of the nuclei. These will approach each other with increasing velocity at first, as long as they are in the attractive region of the potential; then they will approach each other with decreasing velocity, come to a momentary standstill and separate again, finally attaining the same velocity with which they collided. They will both remain unexcited. This sequence of events will occur if the process is adiabatic. Assuming nonadiabatic behavior,

there will be a certain probability that one of the atoms is excited and the velocity of separation is smaller by an amount equal to the excitation energy. The nonadiabatic behavior is, therefore, a jump from one energy level to another.

Knowing these energy surfaces, it is not difficult to give the approximate condition for adiabatic behavior. During the period h/E of the electronic motion the change in the potential V must be small as compared with the energy necessary to excite an electron: $(h/E)vdV/dx < E$. Landau and Zener developed an expression for the transition probability from one level to the other in the case of certain simple shapes of the potentials and this expression will play an important part in the paper of Noyes and Henriques. It shows that the transition probability is a very sharp function of the quantities involved. It can increase by an extremely large factor for a comparatively small increase in the parameters.

The first set of relevant experiments which may be brought up in this connection concern the excitation of atoms by impact of other atoms. In this case E is relatively large; and we must expect adiabatic behavior. Although the experimental material is unfortunately rather scarce, it is evident that, in agreement with the expectation, the excitation by atomic impact has a very low yield. Beeck, Dopel, Gailer, and Holzer have performed such excitation experiments and the excitation seems to be quite unobservable up to velocities of about 150 volts where it sets in, according to Holzer, with a very small cross section.

We know much more about the reverse process, i.e., the so-called collisions of the second kind, than we do about excitation by atomic impact. This process may be readily observed as the phenomenon of the quenching of fluorescence by foreign gases. In this case the system is first on the upper curve and goes over to the lower curve (when energy is plotted against internuclear distances).

In the most simple cases the cross section is very low for this process, about 1/30 of the gas kinetic cross section. Both experiments on Hg and on Na illustrate this, if the luminescence is quenched with noble gases. This means, of course, that the cross section for the reverse process is extremely small according to well-known considerations using the principle of detailed balance. It is smaller in the ratio of the kinetic energies before and after the collision, which is about 100 to 1. Thus the calculated cross section for the excitation process is only 1/3000 of the gas kinetic cross section and the adiabatic hypothesis is well obeyed. However, the cross section for excitation increases strongly with increasing excess energy of the impinging atom.

The quenching cross section for molecules is already very much greater than for atoms of noble gases. The smallest one is that of N_2 against Hg and is $\frac{1}{6}$ of the gas kinetic cross section. The other known cross sections are all gas kinetic or larger. Two circumstances must be remembered, however; first, that the cross section for the reverse process, in which we are mainly interested, is about 100 times smaller—increasing, though slowly, with energy. Second, that the observed cross section is really the sum of very many cross sections since the electronic excitation energy originally present can be distributed in very many more ways among vibrational, rotational, etc. degrees of freedom in the final state than it could be distributed in the initial state. Thus the adiabatic hypothesis is reasonably well obeyed in these cases also.

The situation becomes radically different if we consider not transitions from the lowest to a higher surface, but transitions between a pair of closely spaced surfaces. The cross sections are in this case often greater than the gas-kinetic, cross section by a very large factor and Beutler, among others, has shown that they increase very strongly with decreasing distance of the levels. This is, of course, in qualitative agreement with our formula, but it says at the same time that under these conditions we are very far from a fulfillment of the adiabatic hypothesis. It is customary in this connection to point out that CO and O_2 which strongly quench Hg radiation have probably electronic excitation levels at 4.75 and 4.68 volts, while the Hg excitation energy is 4.86 volts.

I think that these considerations show that the adiabatic hypothesis can be expected to hold in many cases—not, however, generally. In general, the more complicated a system is, the more electronic excitation levels will be present and the chances for a resonance will be correspondingly

increased. This can either hinder the reaction—a case which has been much discussed—or it can make reactions possible which would not be possible otherwise. All cases of chemiluminescence belong to this latter class since, in these cases, there is an electronic excitation in the reaction products while there is none in the initial substances. One group of such reactions already considered in more detail—the chemiluminescence of Na induced by the reaction between Na and a halogen—has been carefully investigated by Polanyi and co-workers, especially Schay, and discussed recently very thoroughly from another point of view by Evans and Polanyi.[17]

James Franck, *University of Chicago:* I do not understand why one should stress the difference between an adiabatic and nonadiabatic process. In chemistry the important thing is the relative positions of the nuclei with respect to each other.

In the impacts between two particles, a transition can occur when the potential curves (energy plotted against internuclear distance) come near to each other. A mixture of helium and mercury at high temperatures gives an emission of light, but at low temperatures helium does not quench excited mercury atoms. If the nuclei are close enough together, the curves will cross and electrons can move to a new state.

John L. Magee, *University of Wisconsin:* In connection with the reaction

$$Na+Cl_2 \rightarrow NaCl+Na^*$$

which Professor Wigner has discussed I should like to point out that the luminescence is to be expected even for an adiabatic process. This is seen when the splitting of the energy surfaces due to effect of the p state of the chlorine atom is considered. The reaction occurs in a plane since it involves only three atoms, and so the electronic states of the reaction system are classified as even or odd with respect to this plane. This symmetry is preserved throughout the reaction. The resulting NaCl molecule is in a Σ state which is even. Thus for reactions which occur in an odd state the sodium atom which is formed must be excited. The even state is doubly degenerate, and thus for adiabatic behavior one of these states will also lead to excitation of the sodium atom. Professor Wigner points out that the surface for the system $Na_2^+ - Cl^-$ crosses the surface for $Na_2 - Cl$ at a large distance and the other even state which would adiabatically lead to a normal sodium atom is probably nonadiabatic due to this crossing.

The relative importance of these three surfaces for the reaction will depend upon the relative activation energies. At any rate the luminescence is not very surprising, since two of the possible electronic states must lead to an excited sodium atom adiabatically and the third most likely yields the same products.

Gregory Breit, *University of Wisconsin:* The motion of the nuclei is just as important as the shape of the energy surface in determining whether or not the reactions are adiabatic.

E. P. Wigner, *Princeton University:* I think that the point of view which I presented is very similar to Professor Franck's. Indeed, the purpose of the approximate formula which I mentioned is to provide a more quantitative background to the phenomena which were just brought up. There are only two minor additions which I would like to make to his remark: First, I believe that it is very infrequent that the lowest energy level is crossed or even very strongly approached by another one and that such a crossing or very strong approach, whenever it occurs, is due to special conditions such as different symmetry properties of the crossing levels or radically different electronic arrangements. Second, I do not think that such crossings are absolutely necessary for nonadiabatic behavior. This will be likely to occur whenever the above-mentioned inequality is infringed. In practice, of course, this will happen most easily if E is small, i.e., if the levels come very close to each other.

[17] M. G. Evans and M. Polanyi, Trans. Faraday Soc. **35**, 178 (1939).

On Intramolecular Diffusion, Quantum Theory, and the Calculation of Unimolecular Velocity-Constants*

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The internal rearrangement of molecules can be considered as the diffusion from one part of a potential energy surface to another. It is suggested that the ordinary diffusion equations might be applied to these cases. The viewpoint is alternative to the method of the activated state. An attempt is made to place this approach on a quantitative basis and to treat it with the help of quantum theory.

PART I

On the connection between quantum theory and the theory of intramolecular diffusion

FROM earlier considerations it is known that it seems natural to describe a chemical process as an intramolecular diffusion.[1] But if this were true, it would seem a very natural conclusion, that all intramolecular motions should be described as diffusion processes.

To investigate this question we start to consider the diffusion of a particle in the absence of forces, and to simplify the mathematics, we shall consider only the unidimensional case. The intensity of flow will be then

$$s=-Dc'$$

($c'=dc/dx$), where x is the space coordinate and c the density of points or the density of probability at place x. The velocity at the place x will be $v=s/c$. We are thus able to calculate the kinetic energy L. To do this, we replace c by ψ^2 and get

$$L=2mD^2(\psi')^2/\psi^2.$$

The energy thus becomes

$$E=2mD^2(\psi')^2/\psi^2+U$$
(U=the potential energy)

and the average energy of the whole molecule is defined as

$$\bar{E}\int\psi^2dx=2mD^2\int(\psi')^2dx+\int U\psi^2dx.$$

We now apply a reasoning used by Hellmann. It is a matter of course that E is completely undefined as long as ψ is an unknown function of x. But we know that atoms and molecules have a tendency to give up energy to the surroundings until they reach a state with minimum energy. This assumption is equivalent to Bohr's postulate of the existence of stationary states. We therefore define ψ so that any variation in its course will, in the first approximation, leave the average energy of the molecule $\bar{E}$ unaltered. If we perform the variation we thus get

$$2\bar{E}\int\psi\ \delta\psi dx=4mD^2\int\psi'\ \delta(\psi')dx+2\int U\psi\ \delta\psi dx.$$

Now the variation and the differentiation in the second integral may be interchanged, and we thus get by partial integration of this integral

$$I_2=-\int\psi''\ \delta\psi dx+|\psi'\ \delta\psi|.$$

But if the integral $\int\psi^2dx$ which represents the total number of particles or the total probability is to have a definite meaning, the integrand must disappear at the limits, and this must be true also in the varied state. Therefore $\delta\psi$ must disappear at both limits and we get

$$\int[2mD^2\psi''+(E-U)\psi]\ \delta\psi dx=0.$$

But as $\delta\psi$ is to be a completely arbitrary function of x this equation can only be true if

$$2mD^2\psi''+(E-U)\psi=0$$

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633. This article replaces the one originally published as a preprint for the symposium.

[1] Zeits. f. physik. Chemie **B33**, 145 (1936).

[2] H. Hellmann, *Einführing in die Quantenchemie* (Leipzig, Deuticke, 1937), p. 49.

is true everywhere. This however is simply Schrödinger's equation if $D=h/4\pi m$, and as this equation has been amply verified by experiment, it must be permissible to describe the intramolecular motions as a diffusion process.

In the case, where we have to do with a diffusion in a field of force, the expression for the intensity of flow becomes a bit more complicated. The expression given originally by A. Einstein becomes with the transformation $U'/RT=V'$, and $\ln \varphi = V$

$$s=-D\varphi^{-1}(c\varphi)'$$

and consequently $v=-D(c\varphi)^{-1}(c\varphi)'$.

Thus our equation for the energy has exactly the same form as before and therefore leads to an equation for ψ of the same form as before if and only if we place $\psi^2=c\varphi$. As $s=0$ when $c\varphi=$ a constant φ obviously plays the role of an activity coefficient. Thus $c\varphi=\psi^2$ may be called the activity at a definite place, and the integral $\int\psi^2dx$ the total activity of the molecule. But this quantity must be the same for all molecules in thermal equilibrium with each other independently of their state. Therefore we must always, in cases where thermal equilibrium must be assumed, normalize ψ so that $\int\psi^2dx=1$ for all molecules, even if their ψ's are different.

(It is well known that equations of the Schrödinger type usually have solutions for which this normalization is possible only for discrete values of E, and that the corresponding functions ψ are all different.)

If now the Schrödinger equation has been solved, we get for the flow s

$$s\varphi=-D(\psi^2)'.$$

But this becomes zero at the limits as we have assumed $\psi=0$ at these limits and the assumption $c\varphi=\psi^2$ therefore cannot be used, when we want to describe a molecule capable of chemical reaction, that is a molecule where the particles really may pass the limits which define the molecule chemically.

Instead of ψ^2 we therefore write y_1y_2 where y_1 and y_2 are two different solutions of the same equation as before:

$$2mD^2\psi''+(E-U)\psi=0.$$

But the integral $\int y_1y_2dx$ must still have a definite value. Now, if ψ_1 is the solution, for which the integral $\int\psi_1^2dx$ has a definite value, the corresponding solution ψ_2 defined by

$$\psi_2=\psi_1\int_0^x\frac{K}{\psi_1^2}dx,$$

where K is the constant differential determinant, $\psi_1\psi_2'-\psi_1'\psi_2$, will be infinite at large positive and negative values of x. Therefore the product y_1y_2 cannot contain ψ_2^2 but it may be of the form $\psi_1(\psi_1-\alpha\psi_2)$ where α is a constant. We get in this case

$$\int_{-\infty}^{+\infty}y_1y_2dx=\int_{-\infty}^{+\infty}\psi_1^2dx-\alpha\int_{-\infty}^{+\infty}\psi_1\psi_2dx.$$

Now ψ_2 obviously is an even function, when φ_1 is uneven and vice versa. Furthermore, for the important case where $2U=px^2$, $\psi_1\psi_2$ disappears as $1/x$ at $x\to\infty$. Therefore the second integral disappears in this case. (It will probably be so in all important cases, but to prove this a more general mathematical investigation is necessary.) If the limits are not both infinite, the integral is not exactly zero, but if only α is very small, we shall not commit any appreciable error by placing $\alpha\int\psi_1\psi_2dx=0$ as it will then in any case be very small as compared to $\int\psi_1^2dx$.

We have thus shown that it is permissible to replace ψ^2 by $y_1y_2=\psi_1(\psi_1-\alpha\psi_2)$ and we get with sufficient accuracy

$$\int y_1y_2dx=\int\psi_1^2dx.$$

Part II

Calculation of reaction velocity

The intensity of flow at any point was given by the equation

$$s=-D\varphi^{-1}(\psi^2)'.$$

This is equal to the unimolecular velocity constant if φ and ψ^2 are correctly normalized, and if we know where the flow is to be measured.

$\ln\varphi=V$ is defined by the differential equation

$$V'=U'/RT.$$

We may therefore put $V=(U-A)/RT$, where A is a constant. We now normalize φ by putting

$$1=a=\int\psi^2dx=e^{A/RT}\int e^{-U/RT}\psi^2dx.$$

This means that we multiply the integral $N_n = \int c_n dx$ with an average activity coefficient $e^{A/RT} = \bar{\varphi}$ so defined, that $N\bar{\varphi} = a = 1$. When ψ is a known function it is possible to perform the integration and thus A may be determined. It is seen that these average activity coefficients are different for different functions ψ, that is, for different states of the molecules, and thus the relative numbers of molecules in different states are different.

The place where we want to know the intensity of flow must be the point which separates two forms of the molecule. The question is how are we to characterize this point. Now if a reaction is going on, the activity in parts of space belonging to one form must always increase with time and in parts belonging to the other form must always decrease with time or vice versa. But this is the same as to say that at the point of separation $\varphi(\partial c/dt) = 0$. At the same time it will be natural to assume that at the point of separation $U' = 0$. But generally $-s' = dc/dt$ so that to assume that at the point of separation c or $c\varphi$ is constant in time is the same as to say that s' is zero.

Consequently we must have at the point of separation

$$0 = \frac{d}{dx}(y_1 y_2)' = y_1 y_2'' + y_1'' y_2 + 2y_1' y_2'$$

or

$$0 = -(E - U) y_1 y_2 + 2mD^2 y_1' y_2'.$$

But x is not infinite at the point of separation and consequently y_1 and y_1' cannot be zero. But we may place $y_2' = \psi_1' - \alpha\psi_2' = 0$ at the point of separation, so that α is defined. If thus we put $E = U$ and $y_2' = 0$ at $x = l$, we get when $x - l$

$$(\psi^2)' = (y_1 y_2)' = y_1' y_2 + y_1 y_2' = \frac{\psi_1'(l)}{\psi_2'(l)} K = \alpha K;$$

$$s = -De^{(A-E)/RT}\alpha K.$$

At the other limit, $x = -\infty$, we get

$$(y_1 y_2)' = 2\psi_1'\psi_1 - \alpha \frac{d}{dx}\psi_1\psi_2.$$

Here $\psi_1'\psi_1$ is certainly zero and the flow at this point will be

$$s = De^{(A-U)/RT}\alpha \frac{d}{dx}\psi_1\psi_2,$$

which is certainly zero as $e^{-U/RT}$ decreases exponentially with increasing values of U and $(d/dx)\psi_1\psi_2$ at least does not increase exponentially. Therefore the loss of activity, which is equal to the relative number of particles lost by chemical reaction, becomes $s(l)$. We thus get for the velocity constant

$$k = -De^{(A-E)/RT}\alpha K,$$

where

$$\alpha K = K \cdot \frac{\psi_1'(l)}{\psi_2'(l)} = K \frac{\psi_1\psi_1'}{\psi_1'\psi_2 + K}; \quad \int \psi_1^2 dx = 1.$$

In most cases $\psi_1'\psi_2$ will be small as compared to K and in these cases we get simply

$$k = -De^{(A-E)/RT}\psi_1\psi_1'.$$

When the Schrödinger equation has been solved, all the quantities in these equations are known, and the problem is thus solved. The actual calculation for a special case $2U = px^2$ will be postponed to a later paper. In this one only two general remarks may be made.

One is, that E is quantized. This appears directly from the derivation.

The second one refers to the quantity A.

We want to determine the heat of activation Q by means of the well-known relation

$$RT^2 \frac{d \ln k}{dT} = Q.$$

Now by definition:

$$\frac{A}{RT} = -\ln \int e^{-U/RT}\psi^2 dx$$

from which

$$T^2 \frac{d}{dT}\left(\frac{A}{T}\right) = -\int Ue^{-U/RT}\psi^2 dx \Big/ \int e^{-U/RT}\psi^2 dx$$

$$= -\bar{U},$$

where $\bar{U}$ means the average value of U. This average value must depend on T and on the quantum number, that is on the function ψ. We thus get

$$RT^2 \frac{d \ln k}{dT} = E - \bar{U} = Q,$$

that is Q depends on temperature. But $\bar{U}$ is not the average potential energy of all the molecules, but only this average for molecules with a given quantum number, corresponding to the value of E.

Discussion

J. O. Hirschfelder, *University of Wisconsin:* This diffusion approach to the theory of reaction rates is similar to that of the activated state method. The concentration of systems on the potential energy surface is given by the ratio of the partition function per unit length along the reaction path, F_t, to the partition function in the initial state, F_i. $c = F_t/F_i$. This formula assumes statistical equilibrium (sufficiently high pressures for the reacting system). In both the diffusion method of Christiansen and the activated state method, this concentration must be calculated. The difference between the two methods appears in the value which they take for the rate of flow, s.

According to the activated state method:

$$s = c\bar{v} = c(kT/2\pi m)^{\frac{1}{2}},$$

where $\bar{v}$ is the average Maxwell-Boltzmann velocity. Professor Christiansen has to evaluate the diffusion constant, D. This difficulty does not appear in the activated state calculations. Instead of starting out from the principles of statistical mechanics (which lead directly to the activated state method) Professor Christiansen proceeds from the ordinary diffusion equations which were derived for an entirely different type of application. It becomes necessary to evaluate the diffusion constant in order to complete the analogy. It is difficult to see how the frequency factor of 10^{13} for a unimolecular reaction can be readily obtained from this presentation. In the activated state method, it arises from the factor kT/h and it is clear that the other factors are of the same order of unity. Then, formally the two theories must give the same results when they are both properly treated since they have arisen from the same set of physical assumptions.

J. A. Christiansen, *Royal Polytechnic Institute, Copenhagen:* From the diffusion equation one actually gets frequency factors of the order of magnitude of 10^{13} and in addition some connection between the activation energy and the frequency factor. But it is true that the frequency factor becomes different in different cases and not exactly like kT/h. I am not quite sure that this is a disadvantage.

K. F. Herzfeld, *The Catholic University of America:* The transition state method gives only the high pressure rate and the use of the diffusion method might permit a calculation of rates in the low pressure region.

J. A. Christiansen, *Royal Polytechnic Institute, Copenhagen:* I consider this one of the advantages of the diffusion method. It assumes a stationary state but not necessarily an equilibrium state.

Henry Eyring, *Princeton University:* The general theory of the activated complex (transition state) method is, I think, well understood. One can treat each system approaching the activated state as a wave packet crossing a potential energy barrier. The various wave packets can then be averaged over energy and phase and the proper rate for each temperature found. The fact that the detailed calculation is laborious and difficult leads one to define an average transmission coefficient κ in the expression for the specific reaction rate $k' = \kappa(kT/h)(F^*/F_n)$. This κ certainly, in general, has a small dependence on temperature and on pressure and is not exactly unity for activated complexes corresponding to a single potential barrier, or exactly one-half when there are two successive barriers of equal height. However, experimental evidence of divergence from such well understood values would be extremely interesting and unfortunately extremely difficult to demonstrate. There is, however, no difficulty in principle in treating such a κ when and if it arises or in anticipating where such divergence is most likely to occur. If one accepts this as a complete theory then any advantage of the interesting proposals of Professor Christiansen must lie in providing a more expeditious method of treating the transmission coefficient which I am convinced is already known within narrow limits.

The Nature of the Critical Complex and the Effect of Changing Medium on the Rate of Reaction*

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The nature of a critical complex may often be related to the change of the rate of the corresponding reaction when the solvent medium is varied by altering either the electrolyte concentration or the dielectric constant. It is necessary to take into consideration the ratio of volume concentration to mole fraction, the possibility of catalytic action, even that due to an ionic charge, and the possibility that the nature of the critical complex may change with changing composition. The critical complex of the bromoacetate-thiosulfate reaction appears to be the two tangent ions. In the ammonium-cyanate reaction there may be a partial de-polarization of the tangent ions. The effect of changing dielectric constant on the solvolysis of tertiary butyl chloride indicates a rather wide separation of the ions in the critical complex.

SOME years ago[1] the author attempted to sort out that which is essential in the various discussions of reaction rates in solution, and to extend as widely as possible the treatment which Brønsted had applied so successfully to the effect of dilute electrolyte solutions on reactions between ions. Recent discussions in this field make desirable a return to the subject.[2]

It is now generally accepted that a reaction goes through a "critical complex," (X), and that the rate is proportional to the concentration of this critical complex, so that for the reaction

$$A+B\rightarrow(X)\rightarrow D+E,$$
$$-dC_A/dt=K'C_X=KC_AC_Bf_Af_B/f_X, \quad (1)$$

in which C is concentration, f is activity coefficient and K' and K are functions of the temperature, but not of composition. K is the specific reaction rate in the standard state medium.

In gaseous reactions f_Af_B/f_X is always sensibly unity. In solutions, however, it is possible to predict the effect of changing medium if the nature of the critical complex is known, or to learn something about the nature of the critical complex from the effect of changing medium on the rate. The success of this method depends upon the fact that the interaction of a pair of molecules with the rest of the solution is nearly independent of their relative positions except for electrostatic forces. This means that the free energy change on the formation of the critical complex varies with changing composition almost entirely through electrostatic forces due to ionic charges, to fixed dipoles in which the charges are widely separated as in the dipolar form of amino acids, or to dipoles which are very near the surface in the reactants but masked in the critical complex as in a "hydrogen bond" between the parts of the complex. The first two effects may be calculated for models which represent many reactions fairly well, and in certain cases the medium is sufficiently characterized by the molar volume, the dielectric constant, and the ionic strength.

When the previous paper was written there were no methods available for calculating activity coefficients of molecules without spherical symmetry. The change in concentration of the critical complex was therefore calculated from the change in the concentration of molecules of one species at a fixed distance from a molecule of the second species by a method developed by Christiansen,[3] and by Eq. (1) any isothermal

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 442. Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] G. Scatchard, Chem. Rev. **1**, 229 (1932).

[2] This paper has been written after the Conference of the Section of Physics and Chemistry of the New York Academy of Sciences on February 24, 1939, at which papers in this field were presented by (a) Eyring and Laidler, (b) J. C. Warner, and (c) P. D. Bartlett; and after the presentation at the Baltimore meeting of the American Chemical Society of the paper by (d) Laidler and Eyring. Although many of the ideas were developed before these meetings and were put forward at the Conference, others arose from these papers and their discussion. The author has attempted to give proper credit, but it must be remembered that citations refer to a memory, which may not be accurate, of an oral report which may differ from the written paper.

[3] J. A. Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

change in C_X/C_AC_B is proportional to the change in f_Af_B/f_X. Since then, Scatchard and Kirkwood[4] have made approximate calculations for a model made up of two equal spheres separated by a distance R, each having an exclusion diameter a for ions and a spherically symmetrical charge $\pm\epsilon$. For the effect of dielectric constant on the reaction between two ions, the two methods give the same answer; for the effect of electrolytes, there is a slight difference beyond the limiting law because Christiansen's method ignores the effect of interaction of the ion atmosphere of one ion upon that of the other. Kirkwood[5] has also developed more rigorous expressions for the effect of changing electrolyte concentration and of changing dielectric constant for the electrostatic part of the activity coefficient of a spherical molecule with any arbitrary distribution of electrical charges. Westheimer and Kirkwood[6] have developed the expression for the effect of changing dielectric constant on an ellipsoid of revolution with charges or point dipoles distributed arbitrarily along the axis of revolution. Eyring and Laidler[2(a), (d)] suggest the use of Kirkwood's spherical model for the critical complex. For most cases of changing dielectric constant the ellipsoid should be more satisfactory because the region most effective for changing dielectric constant in a dipolar molecule is that about the equatorial plane of the dipole and, of course, as close as possible to its axis. It is in just this region that the spherical model excludes too much of the solvent. For large values of the dielectric constant, the much simpler expressions from my earlier paper are probably sufficiently accurate. Similarly, the expressions for the effect of electrolytes is probably sufficient in those ranges where the Debye approximation is satisfactory for activity coefficients. The spherical model of Kirkwood offers very interesting possibilities for special cases.

It should be clear that, although Christiansen used the language of the collision rate theory, his method does not depend at all upon that theory.

[4] G. Scatchard and J. G. Kirkwood, Physik. Zeits. **33**, 297 (1932).

[5] J. G. Kirkwood, J. Chem. Phys. **2**, 351 (1934).

[6] F. H. Westheimer and J. G. Kirkwood, J. Chem. Phys. **6**, 513 (1938). J. G. Kirkwood, Chem. Rev. **24**, 233 (1939), gives the effect of changing electrolyte concentration for an ellipsoidal model.

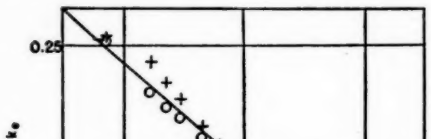

FIG. 1. Relative rates of bromoacetate-thiosulfate reaction at 25°. ● Sucrose-water, —⊙ glycine-water, ⊙ urea-water, ⊙— ethanol-water. The crosses are corresponding values uncorrected for volume effect.

The difference between the collision rate theory and the quasi-thermodynamic or statistical theory lies in the determination of the constant K for the perfect gas phase and not in the variation of the rate with changing medium through a change in f_Af_B/f_X. The difference between Laidler and Eyring's treatment[2(d)] of the effect of changing dielectric constant on the rate of reaction between two ions and my treatment depends upon a difference in model and not upon a difference in theory. They use the spherical model while I used the double sphere. I believe that the double sphere corresponds more closely to the geometry of the critical complex.

There is another factor in the activity coefficients which is generally considered in the treatment of equilibria but is usually ignored in the treatment of rates. In a mixture of nonpolar molecules of different sizes but of the same cohesive energy density, the activities are proportional to the mole fractions and not to the volume concentrations. So the activity coefficients used in Eq. (1) contain a factor inversely porportional to the ratio of the number of moles per liter of the solution to the number in the standard state. These factors cancel for first-order reactions, and the number remaining is one less than the order of the rate determining reaction. It may usually be ignored in the extrapolation to zero concentration of reactants, but it often becomes important in changing solvent, especially if one of the solvents is water. Consideration of this factor accounts for the discrepancy found by La Mer[7]

[7] V. K. La Mer, J. Frank. Inst. **225**, 709 (1938).

for the reaction of thiosulfate ion with bromoacetate ion in sucrose solution. In Fig. 1 are shown the results of Straup-Cope and Cohn[8] in solutions of ethanol, urea and glycine, and those of La Mer and Kamner[9] in a solution of sucrose. The subscript $_0$ refers to water and both corrected and uncorrected results are given. All rates are extrapolated to zero ionic strength by the Debye approximation with $a=6.4$A. The results with other media do not deviate much from a straight line drawn through the water and sucrose solution points, the slope of which corresponds to 5.6A for R in the double sphere model. This seems to be reasonable for the distance between the charges, and there is no reason to assume an electron shift in the formation of the critical complex (*vide infra*). The values for glycine solutions might be expected to fall slightly above the curve as the expression of the effect of such widely separated charges by means of their effect on the dielectric constant should give too small a value. The equation of Kirkwood[8] which takes the distribution of charges into account in more detail should be more satisfactory. It should be noted that the theory does not indicate that the distance necessary for reaction R is the same as the exclusion diameter for ions a. It is true that the computations are simpler when the two distances are equal, but a very considerable change in the distance would make very little difference in the values obtained from the more complicated equations.

In alcohol-water mixtures of low dielectric constant there is a very considerable change in slope at finite salt concentrations which must arise from another cause. The beginnings of this effect are shown in Fig. 1. All the evidence confirms the explanation of La Mer[7,9] that associated ions (in the sense of Bjerrum) are taking part, so that there are six possible reactions:

$$BrAc^- + S_2O_3^=;\ BrAc^- + NaS_2O_3^-;$$
$$BrAc^- + Na_2S_2O_3;\ NaBrAc + S_2O_3^=;$$
$$NaBrAc + NaS_2O_3^-;\ NaBrAc + Na_2S_2O_3.$$

If each of these reactions has the same rate in a solvent of infinite dielectric constant and R is 6.4A, our theory states that in a solution of dielectric constant twenty, the second reaction will go a hundred times as fast as the first, and each of the others will go ten thousand times as fast as the first. Bjerrum's theory[10] states that in the most dilute solution ($0.0002M$ in each reactant) about four percent of the bromoacetate and about two percent of the thiosulfate are in the form of neutral molecules, and about half the thiosulfate as primary ions. The combination of the two theories states that 90 percent of the reaction should go through the neutral molecules, and less than 0.2 percent through the simple ions as in the first reaction listed. The constants so obtained in the range of the experimental measurements are from 500–2000 times the calculated values at zero concentration. The curve, which is determined completely by measurements at higher dielectric constants, crosses a curve through the experimental points at about the middle of the experimental range, but it has a steeper slope. The extrapolation is so enormous that we cannot say that these measurements confirm the theory in solutions of low dielectric constant, but we can say that they are not inconsistent with the theory.

In solutions of low dielectric constant reactions occur through new critical complexes: $(BrAcNaS_2O_3)^=$ for the second and fourth; $(BrAcNa_2S_2O_3)^-$ for the third and fifth, and $(BrAcNa_3S_2O_3)^0$ for the sixth. Thus sodium ion is a catalyst through the fact that it is electrically charged with a sign opposite to that of the reacting ions. A most interesting confirmation of this theory of electrostatic catalysis[11] is the very great catalytic action of La^{+++} cited by La Mer[7] and presumably due to a new critical complex, $(BrAcLaS_2O_3)^0$.

The fading of brom-phenol blue by alkali is another reaction between two anions one bivalent and the other univalent. Amis and La Mer[12] find a greater effect of electrolytes, a

[8] D. Straup-Cope and E. J. Cohn, J. Am. Chem. Soc. **57**, 1794 (1935).

[9] V. K. La Mer and M. E. Kamner, J. Am. Chem. Soc. **57**, 2669 (1935).

[10] The constants for $a=6.4$A are readily obtained from Fig. 1 of R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55**, 1019 (1933).

[11] This theory differs from that of La Mer and Kamner, references 7 and 9, only in recognizing that the complex ions do not greatly outnumber the simple ions in the range of experimental measurements, and that their effect must vanish at zero concentration.

[12] E. S. Amis and V. K. La Mer, J. Am. Chem. Soc. **61**, 905 (1939).

steeper slope for log k *vs.* $1/D$, and a break from this curve at larger values of the dielectric constant, all of which agree in indicating smaller ions. Yet it is highly probable that the two charges of the secondary brom-phenol blue ion are widely separated, and that the third charge in the critical complex is far from either. The probability that this third charge is between the other two, makes a study of the more complicated model of Kirkwood attractive.

The reaction of ammonium ion and cyanate ion to form urea has been much studied by Warner, Svirbely and their co-workers. Since the two ions have equal but opposite charges, the rate of reaction increases as the dielectric constant is decreased. The only complex favored by low dielectric constant has the same composition as the critical complex, so there are none of the complications found with the last reaction. However, the values for the reaction rate at a given value of the dielectric constant depend upon the nonaqueous solvent, and the plots of log K against $1/D$ are not linear for any solvent. The correction to mole fractions makes the curves somewhat worse as to spread and perhaps slightly better as to curvature. Fig. 2 shows the results of Warner and Warrick[13] for mixtures of water with methanol, ethanol and *n*-propanol at 50°C and those of Lander and Svirbely[14] for water-glycol. The results of Warner and Warrick for water-dioxane are almost the same as those with water-propanol.

Part of the deviation from linearity may come from the inaccuracy in the interpolation to zero ionic strength, but this effect is probably not large, and it cannot account for the differences in rate in isodielectric solutions of different composition. The difficulty may well lie in our treatment of the solvent as a homogeneous medium with uniform dielectric constant.[15] Continuation of the measurements to the pure non-

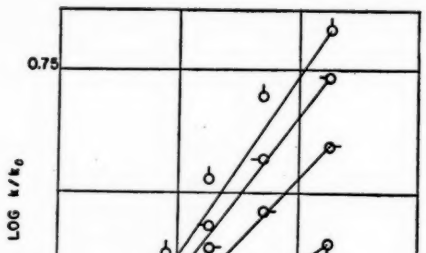

FIG. 2. Relative rates of ammonium-cyanate reaction at 50°. ⊙| Methanol-water, —⊙ ethanol water, ⊙— propanol-water, ⊙| glycol-water.

aqueous solvent in a few cases should indicate whether the difficulty arises from a concentration of the solvent with higher dielectric constant about the ions. If this is the explanation, the measurements in any pair of pure solvents should give the same value for $(\Delta \ln k)/\Delta(1/D)$.

We will interest ourselves in another possible explanation for a change in $(d \ln k)/d(1/D)$ with changing $1/D$ which will probably be found important in some cases, although it cannot be shown at present that it has any bearing upon this particular reaction. The initial slope for methanol-water corresponds to a distance of approach of 2.0A, which seems rather small since equilibrium measurements indicate large radii for each of these ions. This distance is calculated for the double sphere model with unit charge on each sphere, but it would not differ much for a reasonable single sphere or ellipsoid. If the dipolar character were lost in the formation of the critical complex, however, the loss in electrostatic energy for a given distance of approach would be doubled if the two ions had equal radii, and would be increased still more if the two radii were unequal. So the distance of approach necessary for reaction might be doubled or more for the same effect of changing dielectric constant. It is probable that the critical complex is intermediate between the fully charged dipole and the completely nonpolar form. For simplicity we will assume that the two charged spheres

[13] J. C. Warner and E. L. Warrick, J. Am. Chem. Soc. **57**, 1491 (1935). The most concentrated methanol point is from W. J. Svirbely and A. Schramm, *ibid*, **60**, 330 (1938). The use of the volume-concentration-mole fraction relation makes a considerable difference in the energy of activation, or critical increment, calculated by Warner and Svirbely's method of isodielectric variation of the temperature.

[14] J. Lander and W. J. Svirbely, J. Am. Chem. Soc. **60**, 1613 (1938).

[15] The activity coefficients of ions as determined by the solubilities of electrolytes behave qualitatively in the same manner.

approach until they touch, and that then a certain fraction x of the negative charge is transferred from the negative pole to the positive, always retaining spherical symmetry within each sphere. There will be a certain amount of non-Coulombic work associated with this process which we will assume to be independent of the medium. If there is to be a maximum free energy with x between zero and unity the corresponding free energy must be a quadratic function of x near the maximum. The electrostatic free energy is, however, proportional to x and inversely proportional to the dielectric constant. Therefore, in any medium the difference between the energy of a polar form with x near $A/2B$ and the nonpolar form may be written as

$$\Delta F = Ax - Bx^2 + z\epsilon x/RD.$$

When $x = (A + z\epsilon/RD)2B$, ΔF has a maximum

$$\Delta F_{max} = (A + z\epsilon/RD)^2/4B,$$

$$d\Delta F_{max}/d(1/D) = (z\epsilon/R)(A + z\epsilon/RD)/2B = (z\epsilon/R)x.$$

If there were no shift in the position of the maximum, the slope would be $(z\epsilon/R)(A/2B) = (z\epsilon/R)x_0$. Without a more detailed knowledge of the nature of the critical complex we should conclude only that for a reaction with a dipolar critical complex the slope of ln k vs. $1/D$ will become more negative as the dielectric constant decreases. For reactions between two oppositely charged ions, for which the rate increases with decreasing dielectric constant, the curve should become flatter, as it does for the ammonium cyanate—urea reaction. For a reaction of a relatively nonpolar substance through a dipolar critical complex, the curves might be expected to become steeper at low dielectric constants. There is another effect in media of sufficiently low dielectric constants which is ignored in the double sphere model but is taken into account in either of the Kirkwood models. As the dielectric constant of the medium approaches the internal dielectric constant of the solute, the slope of the electrostatic free energy *vs.* $1/D$ decreases except for the case of complete spherical symmetry. Since this effect increases with increasing asymmetry, it will usually be larger for the critical complex than for the reactants so that this effect will usually act in the opposite direction to the effect of the critical complex changing with changing medium.

There are at least two reactions of nonelectrolytes which appear to occur through the polarization of an alkali halide. The Menschutkin reaction has been discussed by Stearn and Eyring[16] from a similar point of view. Another such reaction is the solvolysis of tertiary butyl chloride. Olson and Halford[17] explain the rate of this reaction quite satisfactorily by assuming bimolecular hydrolysis and alcoholysis, each with the activity coefficient of critical complex independent of the solvent composition. As shown by Bateman, Hughes and Ingold,[18] however, the relative amounts of ether and alcohol do not correspond at all with the relative rates of alcoholysis and hydrolysis so calculated. As a matter of fact the relative quantities are much more nearly proportional to the ratios of the mole fractions of alcohol and water present. Moreover, it is extremely difficult to picture a critical complex whose activity coefficient is independent of the solvent composition. Bartlett[2(c)] shows that the results can be explained equally well by a critical complex which has the same activity coefficient as the water, or as the alcohol. Such a critical complex also seems very improbable.

Figure 3 shows the logarithm of the reaction rate, treated as first order, plotted against the reciprocal of the dielectric constant. The points for water-methanol mixtures fall very closely on a straight line, and those for water-ethanol come as close to a straight line as those for ionic reactions. The single points for water-dioxane and water-acetone, where only hydrolysis can occur, fall close to the water-methanol line. The slope of the water-methanol line corresponds to two ions with diameters of 2.5A separated by a very large distance, or by two tangent spheres with diameters of 1.25A. The latter value seems too small, so we may suppose that the critical complex consists of two ions of intermediate size separated by a few molecular

[16] A. E. Stearn and H. Eyring, J. Chem. Phys. **5**, 113 (1937).
[17] A. R. Olson and R. S. Halford, J. Am. Chem. Soc. **59**, 2644 (1937).
[18] L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc. (London) 881, (1938).

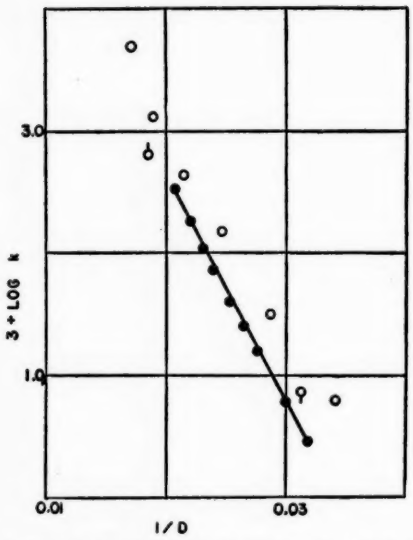

FIG. 3. Rates of solvolysis of tertiary butyl chloride at 25°. ● Methanol-water, ⊙ ethanol-water, ⊙ dioxane-water, ⊙ acetone-water.

diameters. This peculiar picture of a critical complex made up of two separated parts depends upon our custom of picturing the solvent as a continuous background medium. Actually the critical complex must include the solvent molecules between the ions, but the nature of those molecules does appear to make but little difference. The reaction appears to occur when any molecule blocks the reunion of the ions. If the next step of the reaction is the inversion of the organic ion to react with a solvent molecule on the side opposite the chloride ion, this picture corresponds closely to that of Ingold and Hughes for this reaction, and it is not difficult to see that the relative amounts of alcoholysis and hydrolysis should depend largely upon the relative amounts of alcohol and water.. The effect of electrolytes upon this reaction, and particularly the variation of their effect with changing dielectric constant, should give very interesting information.

The results of Farinacci and Hammett[19] for the solvolysis of benzyhydryl chloride show that the dielectric constant is a very crude measure of the effect of solvents on this reaction, and also indicate a very interesting inhibiting effect of nitrobenzene and acetone, which may perhaps be explained by the highly polar, doubly bound oxygens competing with those of the hydroxyl groups for the positions where the latter can react. The reaction is not so simple that definite conclusions should be drawn from a few measurements.

The correlation of reactions of higher order with gas phase reactions, or the calculation of absolute reaction rates requires a more detailed theory of solutions by which we can calculate the vapor pressure of the critical complex from some one solution or, in other words, calculate the free volume of one solution. Even with the present development of the theory of solutions, however, it is possible to learn much from the relative rates of reaction in different solutions.

[19] M. T. Farinacci and L. P. Hammett, J. Am. Chem. Soc. **59**, 2542 (1937).

DISCUSSION

Victor K. LaMer, *Columbia University:* I am not convinced that Professor Scatchard's suggestion that mole fraction activity coefficient should be employed in place of volume molar coefficients in the Christiansen-Scatchard equation, will suffice to eliminate all of the discrepancies between the experimental data and this simple form of the electrostatic theory of reaction rates in the range of dielectric constant for which it is intended. The correction term (minus log $V_0/18$) does indeed bring the LaMer-Kammer sucrose data into much better agreement but as Professor Scatchard points out it also renders the agreement between different solvents for the NH_4CNO reaction worse.

As I pointed out recently[20] when an ion is immersed in a glycine-H_2O solvent, the ion will certainly be surrounded with the more polarizable glycine rather than with water. On the other hand in a sucrose-H_2O solvent, it will be surrounded with H_2O.

This should affect the value of the Born parameter and also the value of D in the immediate neighborhood of the ion. Obviously the rate of a reaction should be more sensitive to the

[20] V. K. LaMer, J. Frank. Inst. **225**, 709 (1938).

value of D in the immediate neighborhood of the colliding ions than to the averaged bulk D which must be substituted in the equation. In his calculations upon the rates of the associated ion reactions, Professor Scatchard makes the primary assumption that they are all equal at $D=\infty$. An approximate measure of these rates can be obtained by extrapolating a tangent of the log k ($\kappa=0$), $1/D$ curve of Dr. Tomlinson's data[21] for bromoacetate-thiosulfate to $D=\infty$ for the various regions of dielectric constant. At $D=20$, where the reaction may be presumed to involve $Na_2S_2O_3^0+NaBrAc^0$, but in any case certainly $BrAc^-+NaS_2O_3^-$, the extrapolated value for k is surely less than for the reaction $S_2O_3^=+BrAc^-$.

Further evidence that the associated ion reactions cannot have the same rates at $D=\infty$ as the free ion reactions, may be obtained from some recent unpublished determinations by Dr. E. S. Amis in our Laboratory on the rate of fading of bromphenol blue ($2\times10^{-5}M$) in 0.09 M NaOH in water-glycol mixtures. These data indicate clearly that there is a critical dielectric constant at which the reaction changes with surprising abruptness from the type:

$$Br\Phi B^=+OH^-(z_Az_B=2)$$

to the type

$$NaBr\Phi B^-+OH^-(z_Az_B=1).$$

When log k at $\sqrt{\mu}=0.3$ is plotted against $1/D$[22] the four new points at $D=78.5$, 71.4, 68.1, 64.9 lie upon a straight line of slope -185 intersecting the straight line, for the second group of four points extending to $D=5$, at $D=64.5$. The ratio of the slopes is 2.04, corresponding to a change in z_Az_B from 2 to 1. When the log k values are extrapolated to $\sqrt{\mu}=0$, using $a=5$A in the Debye function, the same linear character against $1/D$ is observed except that the slope ratio becomes 1.84. Correction to mole fraction coefficients yields a slope ratio of 1.74.

However, none of these calculations is correct, if below $D=64.5$, the BrΦ blue ion exists as $NaBr\Phi B^-$ as the abrupt change in slope indicates. Extrapolating below $D=64.5$ on the assumption of monovalent rather than divalent ions, yields a slope ratio of 2.02, which is good evidence for the postulated change in mechanism.

Extrapolation of these data to $D=\infty$ yields a value of k 1000 times greater for the divalent than for the monovalent ion reaction.

It is suggested that the neutralization of one of the charges renders the ion more stable to attack by OH^-.

In this connection we wish to correct an error of a factor of 2.3 which crept into the calculations in the Amis-LaMer paper.[22] The (r_A+r_B) values of 2.81 and 3.43A calculated for ethyl and methyl alcohol additions should be divided by 2.3 The Born parameter in these alcohols and glycol-H_2O mixtures consequently has the rather low value of 1.2 to 1.5A. Values as low as this have been obtained for the solubility of thallous iodate in alcohol-water mixtures (LaMer-Goldman).

G. Scatchard, *Massachusetts Institute of Technology*): The only purpose of correcting to mole fractions is the determination of that activity coefficient factor which ought to be explained by physical theories. I discussed the ammonium cyanate reaction largely to show that the correction does not make a complex set of data correspond to a simple theory.

Professor LaMer's new information about the fading of bromphenol blue makes this reaction much more difficult to explain. The slope seems too steep for any electrostatic theory, and two intersecting straight lines are contrary to any current theory of solutions. Perhaps the interpretation of this reaction should await the more extended measurements which Dr. LaMer has promised.

A simple interpretation of $d\log k/d(1/D)$ is permissible only when two conditions are simultaneously fulfilled. Practically all of each reactant must exist in a simple form, and practically all of the reaction must go through this form. It is almost certain that the first condition is not fulfilled in the case of the thiosulfate-bromoacetate reaction in solvents of low dielectric constant. I repeat that these measurements are consistent with the values of the rates I used. Moreover, in his Franklin Institute paper, Professor LaMer cites measurements with bromoacetic esters which confirm the order of magnitude of the rate when a neutral molecule is involved.

[21] V. K. LaMer, J. Frank. Inst. **225**, 709 (1938), Fig. 5. Hazel M. Tomlinson, Dissertation, Columbia University, Fig. 2.

[22] Fig. 5, Amis and LaMer, J. Am. Chem. Soc. **61**, 905 (1939).

On the Rate of Ionization in Aqueous Solution of the Carbon-Hydrogen Bond in Aliphatic Compounds*

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The rate at which the carbon-hydrogen bond ionizes to give protons is studied by exchange with deuterium oxide. A base catalyst such as OD^- ion is used. A large number of data are correlated in terms of the rate constants k at 25°. In some cases the calculations required to bring the data to comparable conditions are only approximate. The data are restricted to aliphatic compounds and include measurements on nitrohydrocarbons, acetone, acetaldehyde, acetic acid, acetonitrile, methyl sulfonic acid, halogenated compounds and hydroxl compounds. The velocity constants of ionization range from 10^3 to 10^{-7}, and the order in which the various substituents affect the rate of the CH ionization is given. The influence of substitution on the ionization constants of carboxylic acids has long been studied from the standpoint of thermodynamics. The ionization of CH is a simpler process than the ionization of COOH and it should be possible to learn more of the mechanism through kinetics.

AT THE meeting of the Faraday Society in September 1937 C. L. Wilson[1] gave a report on the ionization rate of carbon-hydrogen bonds and some weeks later at the symposium on deuterium of the Bunsengesellschaft, Ingold and Wilson[2] summarized our knowledge of exchange reactions of light and heavy hydrogen. It is proposed to deal only with a small section of the problems discussed in these reports. We will restrict ourselves to the ionization of the C−H bond in the most simple aliphatic compounds and discuss only exchange reactions in D_2O catalyzed by bases; for base catalyzed reactions alone bear a direct simple relation to the velocity of ionization. During the last few years we have been interested in the deuterium exchange of these compounds and we will try in the following paper to compare the influence of different substituents in methane on the ease of this ionization. For a comparison we must, for the most part, use our own measurements on the velocity of deuterium uptake. But in some important cases we will supplement and compare our results with those obtained by other authors or by other methods.

It is well known that other methods exist for measuring this ionization rate. The direct method of electrical conductivity measurement is available only in the special case of nitrocompounds and, this, indeed, is very fortunate, since the ordinary exchange methods cannot be applied here. Moreover there are many reactions, such as halogenations, tautomerizations, racemizations, aldol condensations and other similar processes, the velocity of which is determined by the carbon hydrogen ionization. It is often possible to draw conclusions concerning the ionization rate from the velocity of these reactions.

It is generally agreed that the base (in the Brønsted sense) catalyzes the exchange of light hydrogen and deuterium by removing a proton from the compound, and that the solvent D_2O (or another deuteron-donator) returns a deuteron at the position where the proton was removed. In the case of all compounds which will be considered here with the exception of the nitroparaffins in alkaline solution, the hydrogen is much more slowly removed from the compound than it is returned. This is shown by the very low degree of ionization of these compounds at equilibrium. Therefore the rate of ionization is equal to the rate of formation of the monosubstituted compound. We will call this velocity the "deuterium exchange rate" even in the case, where the compound contains several equivalent hydrogen atoms as for example acetone. The deuterium exchange rate depends on the nature of the catalyzing base. In most of our experiments the base used was the OD^- ion, so we will, if possible, relate all our velocities to this base and give the ionization rate constants with

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] C. L. Wilson, Trans. Faraday Soc. **34**, 175 (1938).

[2] C. K. Ingold and C. L. Wilson, Zeits. f. Electrochem. **44**, 62 (1938).

respect to $1n$ OD^- concentration and 25°C (calculated with natural logarithms). In cases where no measurements with this base at 25°C were available, we tried to obtain approximate values by calculations from results obtained at other experimental conditions. If the experiments were carried out with OH^- ions and not with OD^- ions, we raised the value by about 40 percent, an amount which Wynne-Jones[3] and La Mer[4] have found in some special cases. In the case of measurements at higher temperatures, such as with acetic acid, log k was extrapolated linearly against $1/T$ to 25°C. Exchange reactions carried out at lower OD^- concentrations were calculated assuming their velocities to be proportional to the OD^- concentration. Consequently the accuracy of the figures given in the following sections varies greatly and is sometimes difficult to estimate. In several cases, also velocity constants for CH_3COO^- or water molecules as catalyst are given.

1. Nitromethane

We place nitromethane at the head of our discussion on account of its especially high tendency to C−H ionization. Pedersen[5] showed that in alkaline solutions the velocity of neutralization which can be followed at 0° by electrical conductivity measurement, is equal to the rate of this ionization. Maron and La Mer[4] measured the velocity in light water and found $k=237$ min.$^{-1}$ for $1n$ OH^- concentration at 0°C. We can obtain an approximate value for $1n$ OD^- concentration at the same temperature by raising this value by approximately 40 percent, a factor found to hold for *nitroethane*, and assuming the same activation heat of 11.5 kcal. We find at 25°C, $k=2\cdot10^3$ min.$^{-1}$.

This value agrees to some extent with results obtained by Junell.[6] He did not determine the concentration of ions by conductivity measurements but by the quantity of bromine used, when an excess of strongly acid bromine solution was added to the alkaline medium, in which the ionization proceeded. Since however this method is not free from objections, it is possible to account for the observed differences.

These objections do not hold for a measurement of the ionization velocity with the acetate ion as catalyst, because in this case the bromination can be followed in a buffer solution of acetic acid and an acetate. It is to be expected, that in this case the rate of bromination will correspond exactly with the rate of ionization (see acetone). The velocity constant, k, at 25°C and $1n$ acetate concentration was found to be $4.0\cdot10^{-3}$ min.$^{-1}$ in D_2O and $4.5\cdot10^{-3}$ min.$^{-1}$ in H_2O.[7,*]

The strong tendency of the nitroparaffins to C−H ionization can be explained from a quantum-mechanical viewpoint as a resonance effect between the two (mesomeric) forms of the ion: $^-CH_2NO_2 \leftrightarrow CH_2=NO_2^-$. In this manner the heat of ionization is lowered.

2. Acetone

In a dilute solution of acetone in deuterium oxide containing KOD, the exchange of light and heavy hydrogen proceeds quite rapidly. Since for a measurement of the reaction rate a separation of acetone and water is necessary and since this separation requires time, only very dilute alkali solutions (<0.01 normal) can be used. The separation of acetone and water was effected by distillation and the amount of deuterium taken up by the acetone was determined by drying and burning it. The velocity was found to be proportional to the OD^- concentration and the velocity constant of the exchange, i.e., of the ionization at $1n$ OD^- concentration was 14.5 min.$^{-1}$ at 25°C.[8]

It is interesting to compare this value with the velocity constant of the base catalyzed halogenation of acetone. Lapworth[9] has shown that the halogenation of acetone catalyzed by acids or bases, is independent of the concentration of halogen, from which it follows that the rate determining step of halogenation is a transformation of the ketone into a reactive form. There are good reasons to believe that in the case of base catalysis this reactive form is the ion

[3] K. F. Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).
[4] S. H. Maron and V. K. La Mer, J. Am. Chem. Soc. **60**, 2588 (1938).
[5] K. I. Pedersen, Dissert. Kopenhagen (1932).
[6] R. Junell, Dissert. Uppsala (1935).
[7] O. Reitz, Zeits. f. physik. Chemie **A176**, 363 (1936).
* The figure given by Reitz is calculated with decadic logarithms.
[8] W. D. Walters and K. F. Bonhoeffer, Zeits. f. physik. Chemie **A182**, 265 (1938).
[9] A. Lapworth, J. Chem. Soc. London **85**, 30 (1904).

$[CH_3COCH_2]^-$ resulting from the ionization of the CH bond. Now the quantitative measurement of the rate of halogenation is not as simple in the case of base catalysis as in the case of acid catalysis on account of side reactions which may take place in alkaline solutions and on account of the reaction of the halogen with the alkali itself. Nevertheless, Dawson and Key[10] succeeded in calculating from their measurements the rate constant of the iodination of acetone for 1 normal OH^- concentration at 25°C and found it to be 25 $min.^{-1}$.

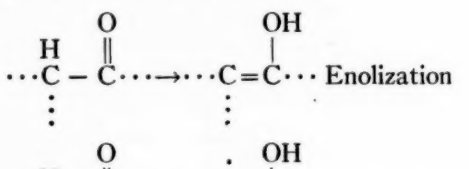
This value although of the same order of magnitude as the value given by the exchange experiments, is almost twice as high. The difference becomes more noticeable when we consider that the iodination experiments were carried out with OH^- ions as catalyst and the exchange experiments with OD^- ions. We will therefore raise the iodination constant by 40 percent in order to get a value that is really comparable. In this manner we obtain a velocity constant of approximately 35 $min.^{-1}$ for the iodination catalyzed by OD^- ions. It is possible that the difference between the rates of iodination and exchange can be explained in the following way. Equality of both reaction constants is only to be expected if the product of iodination is the monosubstituted product. Indeed in the case of acid catalysis CH_2ICOCH_3 is formed, but there are reasons to doubt this for base catalysis. As we will show later it is very probable that in this case higher substituted products such as CI_3COCH_3 are formed. Therefore, it is very reasonable to suppose that the velocity constant for the iodination (as measured by the change in iodine concentration) can be about three times as high as the velocity constant of ionization.

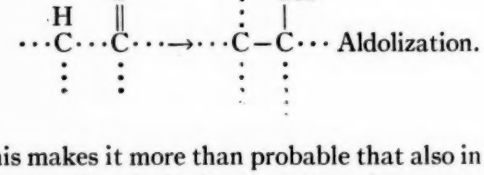
The easy ionization of the C−H bond of acetone can be explained in a manner similar to that of the nitroparaffins. The ion formed by this ionization process is a resonance system which is represented by the two formulae

$$^-CH_2-COCH_3 \leftrightarrow CH_2=CO^--CH_3.$$

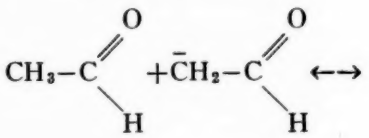
3. Acetaldehyde

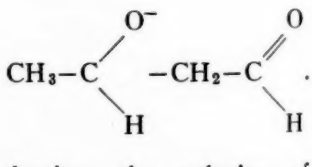
In a dilute solution of acetaldehyde in deuterium oxide containing KOD there is a rapid condensation reaction in which aldol is formed. This reaction proceeds more quickly than in the case of acetone where condensation also takes place. The primary aldol formed was isolated by ether extraction and did not contain any deuterium in the carbon-hydrogen linkage, as opposed to the diacetone alcohol which is the condensation product of acetone.[11] From this we can define an upper limit for the velocity of ionization of acetaldehyde. On the other hand, we have to consider that the mechanism of aldol condensation has a very definite formal resemblance to the mechanism of enolization which is expressed by the formulae





This makes it more than probable that also in the base catalyzed aldolization the primary step is given by the ionization and that the reaction then proceeds as follows:





Assuming this mechanism the velocity of aldolization must also be a lower limit of the velocity of ionization. We have therefore to conclude that the velocity of aldolization is identical with the velocity of ionization and that every acetaldehyde ion formed immediately gives aldol.[11] This assumption agrees with the statement of Bell[12] that the rate of aldolization is of the first order with respect to the acetaldehyde

[10] H. M. Dawson and A. Key, J. Chem. Soc. London 543, 2154 (1928).

[11] K. F. Bonhoeffer and W. D. Walters, Zeits. f. physik. Chemie **A181**, 447 (1938).

[12] R. P. Bell, J. Chem. Soc. London 1637 (1937).

since the rate determining process is the ionization. The velocity constant given by Bell* for $1n$ OH^- concentration (linearly extrapolated) is 8.0 min.$^{-1}$ at 25°. For comparison we must raise that value by about 40 percent, and we obtain the constant 11 min.$^{-1}$ for $1n$ OD^- concentration.

Acetaldehyde and acetone show therefore no appreciable difference in their ionization velocity.

4. Acetic Acid

In a dilute solution of an acetate in deuterium oxide containing an excess of KOD there is, at room temperature, no exchange of hydrogen and deuterium at the carbon atom. Exchange begins only at higher temperatures and requires many hours at 100°C. The process takes place between acetate ions and deuteroxylions. The rate of reaction was measured between 77°C and 206°C by determining the deuterium content of the salt.[13] This was obtained in a mixture with KCl after neutralization of the alkali and removal of the solvent.

At 100°C the velocity constant† was $1.8 \cdot 10^{-3}$ min.$^{-1}$ for $1n$ OD^- concentration. The constant at 25°C was extrapolated with the empirical equation

$$\log_{10} k_{CH_3COO^-,\,OD^-} = 10.2 - \frac{22{,}000}{4.57T} \text{ min}^{-1}.,$$

from whence

$$k = 1 \cdot 10^{-6} \text{ min.}^{-1} \text{ at } 25°\text{C}.$$

This is a measurement of the influence of the COO^- group, but not of the COOD group. The efficiency of the carboxyl group itself cannot be measured with any certainty. Considering the fact that the second dissociation constant of bivalent acids is much lower than the first constant, if both carboxyl groups are near to each other, it is to be expected that the CH_3 group of the acid molecule will ionize more readily than that of the electrically charged acetate ion. It is possible that the uptake of deuterium shown by a neutral acetate (without alkali addition) is caused by the reaction $CH_3COOH + OD^- \leftrightarrow {}^-CH_2COOH + HOD$. This deuterium uptake was measured and from these measurements[13] the constant extrapolated to room temperature would be about 10^4 times higher than the value for the CH_3COO^- ion given above. This ratio would be higher than the ratio of the first and second dissociation constants of oxalic acid. In view of the uncertainty relating to the interpretation of the experimental results this question must remain open.

On the other hand, it is possible to give a value for *acetamide*.[14] Acetamide dissolved in alkaline deuterium oxide shows hydrolysis and deuterium exchange at the same time. The velocity constant for $1n$ OD^- concentration at 25°C is approximately $1 \cdot 10^{-3}$ min.$^{-1}$ i.e., more than 1000 times higher than that of the acetate ion.

The ionization rate constants of the esters of acetic acid are not yet known, because hydrolysis proceeds much faster than exchange in alkaline deuterium oxide. It is possible to say only that the exchange velocity constant of the methylester of acetic acid is less than 1 min.$^{-1}$. This, however, is not of great significance, since the constant is perhaps very much lower and of the order of the velocity constants of acetic acid and acetamide.

One can assume that the same resonance effects which are responsible for the ionization in the case of carbonyl compounds hold with respect to carboxyl and its derivatives but the reason why the carboxyl is less effective does not seem to be quite clear. On the other hand, it is remarkable that the exchange rate of the acetate ion is not very much higher than that of the methylsulfonate ion and that in the latter case a mesomeric effect should not exist.

5. Acetonitrile

In a dilute solution of acetonitrile in deuterium oxide containing KOD the exchange of hydrogen and deuterium in the methyl group proceeds 30 to 40 times faster than hydrolysis. The acetate formed by alkaline hydrolysis in D_2O contained much deuterium. This could not have been introduced by the exchange of the acetate itself on account of its low ionization rate. Assuming an

* k is calculated by Bell with decadic logarithms.

[13] L. D. C. Bok and K. H. Geib, Zeits. f. physik. Chemie **A183**, 353 (1939).

† The figures given by Bok and Geib have to be multiplied by three, since they give the exchange rate for a particular hydrogen atom of the methyl group and not for any one of the hydrogen atoms. Only the latter corresponds with our definition of exchange rate.

[14] O. Reitz, Zeits. f. physik. Chemie **A183**, 371 (1939).

activation heat of about 20 kcal, the velocity constant of acetonitrile calculated from these experiments carried out at 35°C for 1*n* OD^- concentration at 25°C is $2\text{–}3 \cdot 10^{-3}$ min.$^{-1}$.[14] It is of the same order of magnitude as that of acetamide. The facility of ionization can be explained in the same way as with the former substances by considering the resonance effect of the ion $^-CH_2-CN \leftrightarrow CH_2=CN^-$.

6. Methyl Sulfonic Acid

In a dilute solution of sodium methylsulfonate in D_2O containing an excess of NaOD the exchange between hydrogen and deuterium at the carbon atom is slower than the exchange with potassium acetate under corresponding experimental conditions. In experiments at 100°C Hochberg found the rate constant of ionization to be about $1 \cdot 10^{-3}$ min.$^{-1}$ for 1*n* OD^- concentration.[15]

In order to get an approximate value for 25°C we will assume that the heats of activation for the ionization of the acetate and the methylsulfonate ion are equal. On this assumption the ionization rate of the methylsulfonate ion is about $5 \cdot 10^{-7}$ min.$^{-1}$ at 25°C and 1*n* OD^- concentration.

There is some difficulty here in assuming that resonance phenomena contribute to ionization. The SO linkage in compounds of this type is not a double bond but rather a semi-polar one, S^+-O^- and seems not to permit the existence of mesomeric forms.[16] Nevertheless the tendency to ionization in methylsulfonic acid is not very much less than in acetic acid and makes the existence of mesomeric forms not improbable.

7. Halogenated Compounds

The effect of halogen, hydroxyl or alkyl substitution has been measured only in those compounds which themselves show an appreciable tendency toward CH ionization.* Our knowledge of the influence of halogens is based on experiments with brominated nitroparaffins and acetones.

Junell[6] measured the bromination velocity in a 1*n* acid solution of bromosubstituted nitromethane and nitroethane catalyzed by the H_2O molecule as base. At 35°C he found the following values ($c_{H_2O} = 55.5$)

Nitromethane	Monobromonitromethane	Dibromonitromethane
$k = 9 \cdot 10^{-6}$ min.$^{-1}$,	$k = 2.4 \cdot 10^{-3}$ min.$^{-1}$,	$1.2 \cdot 10^{-1}$ min.$^{-1}$.

Since the temperature coefficient has been measured for nitromethane and dibromonitromethane, we can calculate the corresponding values for 25°C and find

Nitromethane	Monobromonitromethane	Dibromonitromethane
$k = 3 \cdot 10^{-6}$ min.$^{-1}$,	$8 \cdot 10^{-4}$ min.$^{-1}$,	$4 \cdot 10^{-2}$ min.$^{-1}$.

The rate constants with OD^- as base catalyst have not been determined. Therefore we cannot give, for the influence of the halogens, values which are directly comparable with the other substituents. However, in any case it follows from the observations with H_2O as catalyst that the tendency to CH ionization is increased if an halogen is attached to the C atom.

Experiments of Watson and Yates[17] with *bromoacetones* point in the same direction. If we plot the velocity of halogenation of acetone as a function of p_H, the curve has a minimum at $p_H = 4$.[18] In the case of bromoacetones, this minimum occurs at lower p_H values. As a result the minimum for highly brominated acetones in mixtures of water and acetic acid (1 : 1) containing HCl is shifted beyond 1 normal HCl concentration. Monobromacetone shows a minimum between 10^{-2} and 10^{-3} *n* HCl concentration. Assuming the acetate ion to be the catalyzing base and considering the fact that the minimum velocities in the case of acetone and monobromoacetone are not very different, one can deduce, that the basic catalysis is increased by a factor

[15] J. Hochberg, unpublished.

[16] B. Eistert, *Tautomerie and Mesomerie* (Enke, Stuttgart, 1938).

* J. Horiuti and Y. Sakamoto found a slow exchange in chloroform, when treated at 100° with 2.5 volume percent of 0.1*n* KOD solution. (Bull. chem. Soc. Jap. **11**, 627 (1936). They announced a further publication which will perhaps allow the calculation of the velocity constants of the reaction.

[17] H. B. Watson and E. D. Yates, J. Chem. Soc. London 1207 (1932).

[18] H. M. Dawson and N. C. Dean, J. Chem. Soc. 2875 (1926).

of 10 or 100 as the result of substitution by one bromine atom.

We may therefore conclude that also in the case of the OH^- ion as catalyst the velocity of ionization is increased by halogen substitution. The OH^- catalyzed bromination of acetone should therefore immediately give a tribromoacetone. It was shown above that this gives an explanation for the difference observed between the exchange and bromination velocities of acetone. In the case of acid catalysts monobromoacetone is brominated more slowly than acetone, so that monobromoacetone is first formed. This agrees with the general experience that the same substituents have an opposite effect in acid and base catalysis.[19]

The halogens are typical representatives of the so-called "negative" substituents. Their influence is due to an "inductive effect" and must not be confused with the "electromeric" effects of substituents such as NO_2, CO, etc. It is generally assumed that this inductive effect is due to the tendency of a halogen atom, to attract electrons. The bromination experiments show, that this tendency is transmitted to the carbon atom, with which the halogen atom is linked. Hydrogen atoms, attached to the carbon atom, become in this way removable as protons. The bromination experiments conflict with the opposite idea that the carbon atom, acquires a tendency to repell electrons as a result of halogen substitution. According to this theory of the "disintegrated octet" the removal of the hydrogen atoms as protons should become more difficult.

8. Hydroxyl Compounds

The introduction of a hydroxyl group at a carbon atom attached to ionizable H atoms produces the inverse effect to that of an halogen atom. The tendency for CH to ionize is decreased. This was shown in experiments using alkaline solutions of *glycollic acid*.[20] The velocity constant of CH ionization in the glycollate ion at 137°C for $1n$ OD^- concentration was found to be $\sim 5 \cdot 10^{-3}$ min.$^{-1}$; while the corresponding velocity constant of the acetate ion is $3.7 \cdot 10^{-2}$ min.$^{-1}$. The ionization velocity of the hydroxylated compound is about 1/7 that of the unsubstituted compound, at 137°C. Assuming that the difference is caused by a difference of activation energy, the factor becomes about 1/10 at room temperature. Therefore we may take the rate constant of the glycollate ion to be $\sim 1 \cdot 10^{-7}$ at 25°C.

Qualitatively we find a similar decrease when we compare the ionization velocity of *dihydroxyacetone* with that of acetone.[11] The ionization velocity of dihydroxyacetone can be deduced employing the same assumption as with acetaldehyde. A 1 : 1 mixture of dihydroxyacetone and glyceraldehyde in a sufficiently diluted alkali solution gives a straight aldol condensation forming fructose and sorbose. If the condensation is carried out in heavy water, no deuterium is found in the CH linkages of the sugar. Therefore the velocity of condensation should be equal to the ionization rate of dihydroxyacetone. The rate constant of the condensation reaction has not yet been measured, but we know that the reaction is complete in about 40 minutes in $0.02n$ alkaline solution. If we assume that this means that 90 to 99 percent of the condensation is finished in this time, we obtain $k \sim 5$ min.$^{-1}$ at $1n$ OD^- concentration. This must be compared with the value of k for acetone 14.5. We find again a decrease of velocity, caused by the substitution of two hydrogen atoms by hydroxyl groups. The difference seems to be smaller than in the case of acetic acid.

Glyceraldehyde alone gives fructose and sorbose as condensation products in alkaline solution; the velocity of the reaction is about three times smaller than in the presence of dihydroxyacetone. We may consider the ionization at the α carbon atom of glyceraldehyde to be the rate determining step.[11] This gives a value between 1 and 2 min.$^{-1}$ for k under conditions corresponding to the above. The rate is 5–10 times slower than that of acetaldehyde. The rates cannot be compared directly since we have a substitution by a hydroxyl group and a hydroxymethyl group at the same time. As it will be shown in the next section that a methyl group also decreases the tendency to CH ionization, this result is not unreasonable.

The fact, that an OH substitution decreases the tendency to ionization, is unexpected. Having

[19] H. B. Watson, *Modern Theories of Organic Chemistry* (Oxford, 1937); C. K. Ingold, J. Chem. Soc. London 1032 (1930).

[20] K. H. Geib, unpublished.

TABLE I. *Velocity constants of* CH *ionization in aqueous solutions (k given in min.$^{-1}$ at constant base concentration and at 25°C, calculated with natural logarithms).*

COMPOUNDS	CATALYZING BASE			REFERENCES
	OD^- ION 1n	ACETATE ION 1n IN H_2O	$H_2O(c=55.5)$	
Nitromethane	$\sim 2 \cdot 10^3$	$4.5 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	4 5 6 7
Monobromonitromethane	—	—	$8 \cdot 10^{-4}$	6
Nitroethane	$3.3 \cdot 10^2$	—	—	4 6
Acetone	14.5	$1.5 \cdot 10^{-5}$	$5 \cdot 10^{-10}$	8 10 22
Monobromoacetone	—	$\gg 1.5 \cdot 10^{-5}$	—	17
Dihydroxyacetone	~ 5	—	—	11
Acetaldehyde	11	—	—	11 12
Glyceraldehyde	1–2	—	—	11
Acetonitrile	$2\text{–}3 \cdot 10^{-3}$	—	—	14
Acetamide	$\sim 1 \cdot 10^{-3}$	—	—	14
[Acetic acid, undiss.]	$[\sim 10^{-2}]$			13
Acetate ion	$\sim 1 \cdot 10^{-6}$			13
Glycollate ion	$1 \cdot 10^{-7}$	—	—	20
Methylsulfonic acid (ion)	$\sim 2 \cdot 10^{-7}$	—	—	15

regard to the electron affinity of the O atom we would expect the effect of OH to be similar to that of halogens. The experiment appears to show that, besides the "inductive" influence of a substituent, there is yet another influence operative, affecting the atoms in the immediate neighborhood. It is possible that this effect is a steric one, but it is also possible that it depends upon the protophilic nature of the OH^- ion. It may be that this ion sometimes removes a proton from the hydroxyl substituent instead of from a carbon atom and that it is thereby made ineffective.

9. ALKYL GROUPS

The influence of alkyl groups has been measured directly by Maron and La Mer[4] in their investigation of the nitroparaffins. They found the following neutralization velocity constants at 0°C in water.

Nitromethane	Nitroethane	Nitroisopropane
237.6	39.11	2.08 min.$^{-1}$

whereas Junell using the bromination method found the constants

Nitroethane	Nitropropane
35.2	29.2 min.$^{-1}$.

This shows that the substitution by alkyl groups decreases the tendency to CH ionization at the α carbon atom.

This result agrees with the experiments of Ives,[21] who showed that the deuterium exchange in propionate ions is about 15 times slower than the exchange in acetate ions at 100°C.

SUMMARY

We summarize our results in Table I in which the data dealt with in this paper are collected. The values of the first column vary between 10^{+3} to 10^{-7}. The advantage of having many comparable values can be obtained only at the expense of the accuracy of some of the figures.

We can state the following order: $NO_2 \cdots CO \cdots CN, CONH_2, \cdots COO^-, SO_3^- \cdots Cl, (OH, CH_3)$ in which the substituents taken from left to right increase the tendency to CH ionization. The substituents in parenthesis have a decreasing effect.

[21] D. J. G. Ives, J. Chem. Soc. London 81 (1938).
[22] G. F. Smith, J. Chem. Soc. London 1744 (1934).

The Mechanism of Some Chain Reactions*

F. O. Rice and K. F. Herzfeld
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(Received May 8, 1939)

The effect of the new values of the heats of activation on the mechanism of the ethane decomposition is discussed. A modification of the original scheme has been put forward by Küchler and Theile which is examined here in detail.

WHEN we published the paper on the mechanism of certain free radical reactions in 1934,[1] very few heats of activation for elementary reactions were known. Some of our guesses have since proved wrong, and we want to investigate the consequences on the ethane decomposition.

For convenience, we shall reproduce the scheme as given in our original paper (with one additional reaction, No. 10), in which the velocity constant of the nth reaction from left to right will be called k_n, and from right to left, k_n'. See Table I. The concentrations are denoted as follows:

C_2H_6	CH_3	CH_3CH_2	H	CH_4
x_1	x_2	x_3	x_4	x_5

C_2H_4	H_2	C_3H_8	C_4H_{10}
x_6	x_7	x_8	x_9

The following facts have to be kept in mind: (1) The inhibition experiments of Hobbs and Hinshelwood[2] have shown that at least the predominant part of the reaction is a chain. (2) Sachsse[3] has found a [H] of 10^{-11}. With the new heat of activation of 8 kcal. for reaction (4), the speed of this reaction, with a concentration x_1 of C_2H_6, is $10^{9.5}e^{-8/RT}10^{-11}x_1=10^{-3.5}$ in agreement with the over-all measured velocity. Therefore, the hydrogen atoms experimentally found present in the decomposing ethane account for the total reaction, as Steacie[4] has already pointed out. The task before us then is to account for this hydrogen atom concentration.

Küchler and Theile[5] have shown that the fact that the [H] is lower than that calculated by our previous scheme (which is in turn due to the lowered heat of activation of (4)), makes it probable that the chain-breaking process is re-union of the ethyl radicals, and not re-union of the ethyl radicals and hydrogen atoms. They have shown that one still gets the right order for the over-all reaction if one assumes that this re-union is bimolecular, while the primary break of ethane into two radicals has to be assumed to be also bimolecular; this is plausible in view of the simplicity of the ethane molecule. The equation for the over-all reaction which they get is the following:

$$-\frac{d[C_2H_6]}{dt}=k_3\left(\frac{2k_1}{k_{10}}\right)^{\frac{1}{2}}[C_2H_6]=k[C_2H_6]. \quad (1)$$

TABLE I.

No.	Chemical equation
1	$C_2H_6 \rightleftarrows 2CH_3$
2	$CH_3+C_2H_6 \rightleftarrows CH_4+CH_3CH_2$
3	$CH_3CH_2 \rightleftarrows C_2H_4+H$
4	$H+C_2H_6 \rightleftarrows H_2+CH_3CH_2$
5	$H+H \rightleftarrows H_2$
6α	$H+CH_3CH_2 \rightleftarrows C_2H_4+H_2$
β	$H+CH_3CH_2 \rightleftarrows C_2H_6$
7	$H+CH_3 \rightleftarrows CH_4$
8	$CH_3+CH_3CH_2 \rightleftarrows C_3H_8$
9	$2CH_3CH_2 \rightleftarrows C_4H_{10}$
10	$2CH_3CH_2 \rightleftarrows C_2H_4+C_2H_6$

Velocity constant	Heat of activation	
	E	E'
k_1, k_1'	80	8
k_2, k_2'	20	20
k_3, k_3'	49	10
k_4, k_4'	17	25
$\frac{1}{2}k_5, \frac{1}{2}k_5'$	Triple collision	100
$k_6\alpha, k_6'\alpha'$	Small	60
$k_6(1-\alpha), k_6'\beta$	Small	90
k_7, k_7'	Small	90
k_8, k_8'	8	80
k_9, k_9'	8	80
k_{10}, k_{10}'	8	80

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

[2] J. E. Hobbs and C. N. Hinshelwood, Proc. Roy. Soc. **167**, 439 (1938).

[3] H. Sachsse, Zeits. f. physik. Chemie **B31**, 79 (1935).

[4] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).

[5] L. Küchler and H. Theile, Zeits. f. physik. Chemie **B42**, 359 (1939).

They have, however, not discussed this scheme in detail, and we shall do that now.

1. Heats of Activation

We call Q_1 the strength of the C−C bond. This quantity equals E_1-E_1'. If we assume that the heats of activation are equal for the bond between two methyls and between two ethyls, we can say that $Q_1=E_1-E_{10}$. We call Q_2 the energy difference between CH_3+H and CH_4; we assume that Q_2 is also the energy difference between C_2H_5+H, and C_2H_6. We take E_{10} to be 8 kcal.

The differences in the heats of combustion of C_2H_6, and $C_2H_4+H_2$, give the following equation:

$$118=2Q_2-Q_1. \tag{2}$$

Furthermore, the heat of formation of H_2 and the heat of hydrogenation of C_2H_4 give the following equation:

$$136=E_3-E_3'+Q_2. \tag{3}$$

These two equations together give:

$$154=2(E_3-E_3')+Q_1$$

or

$$77=E_3-E_3'+\tfrac{1}{2}(E_1-E_{10}). \tag{4}$$

According to the measured heat of activation we find in Küchler's mechanism,

$$77=E_3+\tfrac{1}{2}(E_1-E_{10}) \tag{5}$$

so that the thermochemical data are in agreement with Küchler's mechanism, provided that E_3' is zero, while any value of the C−C bond strength would do if E_3 were chosen appropriately. The data given in Table II have been proposed.

2. The Constant Factor

One difficulty might be raised against the scheme of Küchler. If the primary decomposition of C_2H_6 is bimolecular, the decomposition of C_2H_5 into C_2H_4+H ought to be bimolecular also. To discuss that problem, we shall sum up the results of the theory (Polanyi, Lindemann, Christiansen, Hinshelwood, Kassel, O. K. Rice). If the natural unimolecular decomposition is slower than the supply of energy by collisions, the first determines the resultant speed; if the rate of supply is smaller, it determines the resultant speed. Now the rate of supply increases, the more degrees of freedom cooperate to bring energy into the bond that is to be broken. If we used the constants applicable for one degree of freedom only, the bimolecular constant would be 10^9, and the rate of the unimolecular decomposition of ethyl could not be larger than a fraction of 10^9, which would make the over-all constant $\frac{1}{2}\,10^9(10^9/10^8)^{\frac{1}{2}}$, ($10^8$ in the denominator being the recombination constant of $2C_2H_5$ with a steric factor of 1/10). This gives only an over-all constant of 10^9, while the experimental constant is $10^{15.7}$. It is therefore necessary that several degrees of freedom cooperate. We are going to assume that six degrees of freedom for ethane and eight for ethyl cooperate; for these we will assume an average vibration frequency of 1000 wave numbers (size of the quantum 2.9 kcal. per mole) for all degrees of ethane and for six of ethyl, while the seventh in ethyl has 1600 (size of the quantum 4.7 kcal. per mole) and the eighth 3000 (8.7 kcal./mole). According to the theory of Kassel[6] and O. K. Rice,[7] if we select the C−C bond strength as 72 kcal., we can get a factor of about 4×10^4 for ethane, and a factor of about 20,000 for ethyl, while if we select a bond strength of 90, the factor for ethane will be even higher so that we might expect a unimolecular decomposition, while the factor for ethyl will be only about 600. We select the former set of values, so that the constant for the energy supply for ethyl is 10^{13}. That the unimolecular constant for ethyl is smaller than that for ethane, where we take the supply constant as 2×10^{13}, is owing to the change in bond type in

TABLE II. *Bond strengths and activation energies in the ethane decomposition.*

Authors	Ref. No.	C−H	C−C	H(or D)+C_2H_6 = C_2H_5+H_2(D_2)	E_3
Rice and Herzfeld	(1)	~95	72–76	17	49
Trenner, Morikawa and Taylor	(*a*)	108	97.6		26.5*
Burton	(*b*)	94.8	72.1		40*
Morikawa, Benedict and Taylor	(*c*)			11	
Patat	(*d*)	102.5			
Steacie and Phillips	(4)			6.3	

* Calculated using Eq. (5).
[a] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).
[b] M. Burton, J. Chem. Phys. **6**, 818 (1938).
[c] Morikawa, Benedict and Taylor, J. Chem. Phys. **5**, 212 (1937).
[d] F. Patat, Zeits. f. physik. Chemie **B32**, 290 (1936).

[6] L. Kassel, J. Phys. Chem. **32**, 1065 (1928).
[7] O. K. Rice, Proc. Nat. Acad. Sci., U. S. **14**, 113 (1928).

the decomposition of ethyl, which necessitates a motion of the hydrogen atoms. The resultant constants are therefore for k_3, 10^{12}, for k_1, 2×10^{13}, and for k_{10}, 10^8. This gives $10^{14.8}$ for the over-all reaction. The [H], x_4, comes out theoretically somewhat lower by approximately the same factor.

We may note that Sachsse gives a somewhat different experimental constant, owing to a different heat of activation.

Discussion

F. O. Rice and K. F. Herzfeld, *Catholic University of America:* The particular modification of our original scheme which is given in this paper is necessitated by Sachsse's low value for the stationary state concentration of hydrogen atoms in the ethane decomposition. Our original scheme will give an over-all unimolecular constant even if the primary reaction is bimolecular, providing we make our original stopping reactions (6α, 6β) three body; however, the low [H] in the case of ethane does not permit us to do this.

The problem arises whether the frequency factor has abnormal values for chain reactions, so that it would be possible to decide from an experimental measurement of the rate whether a given reaction is simple or consists of a chain. We will assume that only first- or second-order elementary reactions occur in the process and that triple reactions are absent. If the frequency factors of the first-order elementary reactions are $A_1, A_2, \cdots$, and those of the second-order elementary reactions are $B_1, B_2, \cdots$, then the over-all frequency factors will always have the form

$$A = A_1^{n_1} A_2^{n_2} \cdots B_1^{m_1} B_2^{m_2} \cdots .$$

For example, in our mechanism for the ethane decomposition we obtained

$$k = k_1^{\frac{1}{2}} k_2^{\frac{1}{2}} k_3^{\frac{1}{2}} k_6^{-\frac{1}{2}}.$$

If we consider a reaction with an over-all order of one,[8] it follows from simple dimensional considerations that

$$n_1+n_2+\cdots=1$$
$$m_1+m_2+\cdots=0$$

as exemplified in the ethane decomposition. This means that if we add the exponents of all the first-order elementary reactions, taking care of their sign, we obtain one if there are equal numbers of second-order factors in the numerator and in the denominator.

We may simplify further by assuming all the A's equal to $A' = 10^{14}$ and all the B's equal among themselves. Then the over-all A would be independent of the frequency factors of the second-order reaction and would be itself equal to A'. Therefore in this case the over-all chain reaction would have exactly the same frequency factor as a single first-order elementary reaction.

Even if we permit triple collisions, this last conclusion is not materially changed. Apart from the exponential, the reaction rates of first order, second order and third order are, $10^{14}x$, 10^9x^2 and 10^5x^3, so that the transition from first to second order multiples the rate by $10^{-5}x$, and that from second to third by $10^{-4}x$. Therefore, if one elementary reaction involves a triple collision instead of a second-order reaction, the over-all reaction has to have one more first-order reaction instead of a second-order reaction on the same side of the fraction line as the triple collision (or vice versa on the other side) to make the order right, and this changes the numerical value only by $\sqrt{10}$.

Actually, one finds chain reactions with a somewhat high value of A and we will discuss this rather astonishing fact by referring to the two types of formula which we find in organic chain mechanisms, namely

$$A = \left(A_1 A_2 \frac{B_1}{B_2}\right)^{\frac{1}{2}} \quad (6) \qquad A = A_1\left(\frac{A_2}{A_3}\cdots\frac{B_1}{B_2}\right)^{\frac{1}{2}}. \quad (7)$$

If an exceptional value of A or B occurs, i.e., if $B_1 = \alpha B_2$, where $\alpha \gg 1$, the value of A is affected only by $\sqrt{\alpha}$; therefore, in order to account for a value of A one hundred times larger than expected, α has to have a value of 10^4. Only if A_1 in Eq. (7) were affected, would the first power of the anomalous factor enter directly. The theories of Eyring, Gershinowitz and O. K.

[8] For an over-all order of 1.5, $\Sigma n = \frac{1}{2}$; $\Sigma m = \frac{1}{2}$. For an over-all order of 2, $\Sigma n = 0$; $\Sigma m = 1$.

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COMPOUNDS	CATALYZING BASE			REFERENCES
	OD^- ION $1n$	ACETATE ION $1n$ IN H_2O	$H_2O(c=55.5)$	
Nitromethane	$\sim 2 \cdot 10^3$	$4.5 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	4 5 6 7
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Acetamide	$\sim 1 \cdot 10^{-3}$	—	—	14
[Acetic acid, undiss.]	$[\sim 10^{-2}]$			13
Acetate ion	$\sim 1 \cdot 10^{-6}$			13
Glycollate ion	$1 \cdot 10^{-7}$	—	—	20
Methylsulfonic acid (ion)	$\sim 2 \cdot 10^{-7}$	—	—	15

regard to the electron affinity of the O atom we would expect the effect of OH to be similar to that of halogens. The experiment appears to show that, besides the "inductive" influence of a substituent, there is yet another influence operative, affecting the atoms in the immediate neighborhood. It is possible that this effect is a steric one, but it is also possible that it depends upon the protophilic nature of the OH^- ion. It may be that this ion sometimes removes a proton from the hydroxyl substituent instead of from a carbon atom and that it is thereby made ineffective.

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C_2H_6	CH_3	CH_3CH_2	H	CH_4
x_1	x_2	x_3	x_4	x_5

C_2H_4	H_2	C_3H_8	C_4H_{10}
x_6	x_7	x_8	x_9

The following facts have to be kept in mind: (1) The inhibition experiments of Hobbs and Hinshelwood[2] have shown that at least the predominant part of the reaction is a chain. (2) Sachsse[3] has found a [H] of 10^{-11}. With the new heat of activation of 8 kcal. for reaction (4), the speed of this reaction, with a concentration x_1 of C_2H_6, is $10^{9.5}e^{-8/RT}10^{-11}x_1=10^{-3.5}$ in agreement with the over-all measured velocity. Therefore, the hydrogen atoms experimentally found present in the decomposing ethane account for the total reaction, as Steacie[4] has already pointed out. The task before us then is to account for this hydrogen atom concentration.

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TABLE I.

No.	Chemical equation
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2	$CH_3+C_2H_6 \rightleftarrows CH_4+CH_3CH_2$
3	$CH_3CH_2 \rightleftarrows C_2H_4+H$
4	$H+C_2H_6 \rightleftarrows H_2+CH_3CH_2$
5	$H+H \rightleftarrows H_2$
6α	$H+CH_3CH_2 \rightleftarrows C_2H_4+H_2$
β	$H+CH_3CH_2 \rightleftarrows C_2H_6$
7	$H+CH_3 \rightleftarrows CH_4$
8	$CH_3+CH_3CH_2 \rightleftarrows C_3H_8$
9	$2CH_3CH_2 \rightleftarrows C_4H_{10}$
10	$2CH_3CH_2 \rightleftarrows C_2H_4+C_2H_6$

Velocity constant	Heat of activation	
	E	E'
k_1, k_1'	80	8
k_2, k_2'	20	20
k_3, k_3'	49	10
k_4, k_4'	17	25
$\frac{1}{2}k_5, \frac{1}{2}k_5'$	Triple collision	100
$k_6\alpha, k_6'\alpha'$	Small	60
$k_6(1-\alpha), k_6'\beta$	Small	90
k_7, k_7'	Small	90
k_8, k_8'	8	80
k_9, k_9'	8	80
k_{10}, k_{10}'	8	80

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

[2] J. E. Hobbs and C. N. Hinshelwood, Proc. Roy. Soc. **167**, 439 (1938).

[3] H. Sachsse, Zeits. f. physik. Chemie **B31**, 79 (1935).

[4] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).

[5] L. Küchler and H. Theile, Zeits. f. physik. Chemie **B42**, 359 (1939).

They have, however, not discussed this scheme in detail, and we shall do that now.

1. Heats of Activation

We call Q_1 the strength of the C−C bond. This quantity equals E_1-E_1'. If we assume that the heats of activation are equal for the bond between two methyls and between two ethyls, we can say that $Q_1=E_1-E_{10}$. We call Q_2 the energy difference between CH_3+H and CH_4; we assume that Q_2 is also the energy difference between C_2H_5+H, and C_2H_6. We take E_{10} to be 8 kcal.

The differences in the heats of combustion of C_2H_6, and $C_2H_4+H_2$, give the following equation:

$$118=2Q_2-Q_1. \tag{2}$$

Furthermore, the heat of formation of H_2 and the heat of hydrogenation of C_2H_4 give the following equation:

$$136=E_3-E_3'+Q_2. \tag{3}$$

These two equations together give:

$$154=2(E_3-E_3')+Q_1$$

or

$$77=E_3-E_3'+\tfrac{1}{2}(E_1-E_{10}). \tag{4}$$

According to the measured heat of activation we find in Küchler's mechanism,

$$77=E_3+\tfrac{1}{2}(E_1-E_{10}) \tag{5}$$

so that the thermochemical data are in agreement with Küchler's mechanism, provided that E_3' is zero, while any value of the C−C bond strength would do if E_3 were chosen appropriately. The data given in Table II have been proposed.

2. The Constant Factor

One difficulty might be raised against the scheme of Küchler. If the primary decomposition of C_2H_6 is bimolecular, the decomposition of C_2H_5 into C_2H_4+H ought to be bimolecular also. To discuss that problem, we shall sum up the results of the theory (Polanyi, Lindemann, Christiansen, Hinshelwood, Kassel, O. K. Rice). If the natural unimolecular decomposition is slower than the supply of energy by collisions, the first determines the resultant speed; if the rate of supply is smaller, it determines the resultant speed. Now the rate of supply increases, the more degrees of freedom cooperate to bring energy into the bond that is to be broken. If we used the constants applicable for one degree of freedom only, the bimolecular constant would be 10^9, and the rate of the unimolecular decomposition of ethyl could not be larger than a fraction of 10^9, which would make the over-all constant $\frac{1}{2}\,10^9(10^9/10^8)^{\frac{1}{2}}$, ($10^8$ in the denominator being the recombination constant of $2C_2H_5$ with a steric factor of 1/10). This gives only an over-all constant of 10^9, while the experimental constant is $10^{15.7}$. It is therefore necessary that several degrees of freedom cooperate. We are going to assume that six degrees of freedom for ethane and eight for ethyl cooperate; for these we will assume an average vibration frequency of 1000 wave numbers (size of the quantum 2.9 kcal. per mole) for all degrees of ethane and for six of ethyl, while the seventh in ethyl has 1600 (size of the quantum 4.7 kcal. per mole) and the eighth 3000 (8.7 kcal./mole). According to the theory of Kassel[6] and O. K. Rice,[7] if we select the C−C bond strength as 72 kcal., we can get a factor of about 4×10^4 for ethane, and a factor of about 20,000 for ethyl, while if we select a bond strength of 90, the factor for ethane will be even higher so that we might expect a unimolecular decomposition, while the factor for ethyl will be only about 600. We select the former set of values, so that the constant for the energy supply for ethyl is 10^{13}. That the unimolecular constant for ethyl is smaller than that for ethane, where we take the supply constant as 2×10^{13}, is owing to the change in bond type in

Table II. *Bond strengths and activation energies in the ethane decomposition.*

Authors	Ref. No.	C−H	C−C	H(or D)+C_2H_6 = C_2H_5+H_2(D_2)	E_3
Rice and Herzfeld	(1)	~95	72–76	17	49
Trenner, Morikawa and Taylor	(*a*)	108	97.6		26.5*
Burton	(*b*)	94.8	72.1		40*
Morikawa, Benedict and Taylor	(*c*)			11	
Patat	(*d*)	102.5			
Steacie and Phillips	(4)			6.3	

* Calculated using Eq. (5).
[a] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).
[b] M. Burton, J. Chem. Phys. **6**, 818 (1938).
[c] Morikawa, Benedict and Taylor, J. Chem. Phys. **5**, 212 (1937).
[d] F. Patat, Zeits. f. physik. Chemie **B32**, 290 (1936).

[6] L. Kassel, J. Phys. Chem. **32**, 1065 (1928).
[7] O. K. Rice, Proc. Nat. Acad. Sci., U. S. **14**, 113 (1928).

the decomposition of ethyl, which necessitates a motion of the hydrogen atoms. The resultant constants are therefore for k_3, 10^{12}, for k_1, 2×10^{13}, and for k_{10}, 10^8. This gives $10^{14.8}$ for the over-all reaction. The [H], x_4, comes out theoretically somewhat lower by approximately the same factor.

We may note that Sachsse gives a somewhat different experimental constant, owing to a different heat of activation.

Discussion

F. O. Rice and K. F. Herzfeld, *Catholic University of America:* The particular modification of our original scheme which is given in this paper is necessitated by Sachsse's low value for the stationary state concentration of hydrogen atoms in the ethane decomposition. Our original scheme will give an over-all unimolecular constant even if the primary reaction is bimolecular, providing we make our original stopping reactions (6α, 6β) three body; however, the low [H] in the case of ethane does not permit us to do this.

The problem arises whether the frequency factor has abnormal values for chain reactions, so that it would be possible to decide from an experimental measurement of the rate whether a given reaction is simple or consists of a chain. We will assume that only first- or second-order elementary reactions occur in the process and that triple reactions are absent. If the frequency factors of the first-order elementary reactions are $A_1, A_2, \cdots$, and those of the second-order elementary reactions are $B_1, B_2, \cdots$, then the over-all frequency factors will always have the form

$$A = A_1^{n_1} A_2^{n_2} \cdots B_1^{m_1} B_2^{m_2} \cdots .$$

For example, in our mechanism for the ethane decomposition we obtained

$$k = k_1^{\frac{1}{2}} k_2^{\frac{1}{2}} k_3^{\frac{1}{2}} k_6^{-\frac{1}{2}}.$$

If we consider a reaction with an over-all order of one,[8] it follows from simple dimensional considerations that

$$n_1 + n_2 + \cdots = 1$$
$$m_1 + m_2 + \cdots = 0$$

as exemplified in the ethane decomposition. This means that if we add the exponents of all the first-order elementary reactions, taking care of their sign, we obtain one if there are equal numbers of second-order factors in the numerator and in the denominator.

We may simplify further by assuming all the A's equal to $A' = 10^{14}$ and all the B's equal among themselves. Then the over-all A would be independent of the frequency factors of the second-order reaction and would be itself equal to A'. Therefore in this case the over-all chain reaction would have exactly the same frequency factor as a single first-order elementary reaction.

Even if we permit triple collisions, this last conclusion is not materially changed. Apart from the exponential, the reaction rates of first order, second order and third order are, $10^{14}x$, 10^9x^2 and 10^5x^3, so that the transition from first to second order multiples the rate by $10^{-5}x$, and that from second to third by $10^{-4}x$. Therefore, if one elementary reaction involves a triple collision instead of a second-order reaction, the over-all reaction has to have one more first-order reaction instead of a second-order reaction on the same side of the fraction line as the triple collision (or vice versa on the other side) to make the order right, and this changes the numerical value only by $\sqrt{10}$.

Actually, one finds chain reactions with a somewhat high value of A and we will discuss this rather astonishing fact by referring to the two types of formula which we find in organic chain mechanisms, namely

$$A = \left(A_1 A_2 \frac{B_1}{B_2}\right)^{\frac{1}{2}} \quad (6) \qquad A = A_1 \left(\frac{A_2}{A_3} \cdots \frac{B_1}{B_2}\right)^{\frac{1}{2}}. \quad (7)$$

If an exceptional value of A or B occurs, i.e., if $B_1 = \alpha B_2$, where $\alpha \gg 1$, the value of A is affected only by $\sqrt{\alpha}$; therefore, in order to account for a value of A one hundred times larger than expected, α has to have a value of 10^4. Only if A_1 in Eq. (7) were affected, would the first power of the anomalous factor enter directly. The theories of Eyring, Gershinowitz and O. K.

[8] For an over-all order of 1.5, $\Sigma n = \frac{1}{2}$; $\Sigma m = \frac{1}{2}$. For an over-all order of 2, $\Sigma n = 0$; $\Sigma m = 1$.

Rice, and particularly the calculations of Gorin, Kauzmann, Walter and Eyring have shown that the A's will probably not differ by more than a factor of 10 from 10^{14}.

On the other hand, it seems improbable that the B's appearing in chain reactions are exceptionally small, i.e., have a very large steric factor.

There appear to be only three possibilities to account for the very large values of the A's in chain reactions.

(1) An A in the denominator might be very small. This would occur for an elementary first-order reaction involving a change of electron state, so that there would be only a small transition probability from the old to the new electron state, as in the case of N_2O. This example will not occur often.

(2) A unimolecular elementary decomposition which ought to go with, for example, $A=10^{14}$, does not receive sufficient energy supply from collisions because at the given pressure not enough degrees of freedom cooperate to form an energy storehouse; the rate determining factor is then the rate of energy supply. This obeys the bimolecular formula but with a value of B that is much larger than the total number of collisions, which a molecule suffers.

For reactions like $H+C_2H_6\rightarrow H_2+C_2H_5$, the B is of the order of the collision factor 10^9 sec.$^{-1}$ (with units atmospheres and room temperature) because their low heat of activation makes the multiplying factor $(Q/RT)^{S-1}/S!$ not much different from one; Q is the heat of activation, and S is the number of degrees of freedom cooperating.

But in the breaking of bigger molecules with a high bond strength, this factor does not matter and might bring a B almost up to the value of A. We say "almost" because otherwise there would be a transition to a unimolecular elementary reaction. Such a B might therefore be $10^9<B<5\times10^{13}$. At the upper limit, if B_1 belongs to such a reaction and B_2 is normal, $B_1/B_2\sim5\times10^4$, which increases the over-all A by a factor of 200.

But then slightly higher pressures will change the order of the over-all reaction from 1 to 0.5.

(3) There exists the possibility of an impurity being present in constant proportion which acts as the real chain breaker instead of the assumed mechanism.

E. W. R. Steacie, *McGill University:* Your activation energy for the decomposition of ethane is rather high. Since the exponential factor and nonexponential factor work against each other it might be possible to lower the activation energy so that the nonexponential factor may be lowered by as much as $10^{1.5}$.

Farrington Daniels, *University of Wisconsin:* The term "frequency factor" has been used in some of the symposium papers to designate the nonexponential factor in the Arrhenius equation. There have been objections to other names proposed for this important term, but this name seems very satisfactory. Are there any objections to adopting the name "frequency factor" for the term s in the Arrhenius equation $k=se^{-E/RT}$?

Victor K. LaMer, *Columbia University:* I proposed the name at the recent meeting of the Faraday Society and agree heartily that it should be adopted.

W. D. Harkins, *University of Chicago:* How does the strength of the carbon-carbon bond in diamond compare with that in ethane?

K. F. Herzfeld, *Catholic University of America:* I am afraid that no one is quite sure.

Farrington Daniels, *University of Wisconsin:* The extent to which one can assign a given energy value to a bond, independent of the rest of the molecule, seems to be one of the important problems in chemical kinetics.

H. Gershinowitz, *Shell Oil Company:* In a recent paper with Dr. Teller, you showed that the reaction $C_2H_6\rightarrow C_2H_4+H_2$ could proceed in one step by the elimination of molecular hydrogen. What is the relation between that process and the chain mechanism you have discussed?

F. O. Rice, *Catholic University of America:* We do not know the relative activation energies of the direct separation of hydrogen from ethane as compared with the chain process. Hinshelwood has measured the rate of decomposition of ethane in the presence of small amounts of nitric oxide but it seems doubtful whether nitric oxide stops the chain completely.

The Reactions Between Methyl Radicals*

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The reactions of methyl radicals with each other and with hydrogen molecules are reviewed. It is shown that the available evidence is consistent with the following statements: Methyl radicals combine only in three-body collisions, the energy of activation of which may be as high as 22 kcal. Methyl radicals do not readily enter into two-body reactions with hydrogen molecules. Most of the methyl radicals in an atmosphere containing a high percentage of hydrogen probably disappear by the reaction $CH_3+H_2+CH_3\rightarrow 2CH_4$, the energy of activation being probably 9 ± 2 kcal. The reaction $CH_3+H_2\rightarrow CH_4+H$ accounts at most for the disappearance of 1 in 10^4 methyl radicals, the energy of activation being $\sim$19 kcal.

EVIDENCE has been presented[1] that the thermal decomposition of acetaldehyde proceeds by a free radical mechanism and not by a simple rupture into stable molecules. It is important therefore to consider the possible reactions in such a chain mechanism in somewhat greater detail than has hitherto been essayed. More especially is this necessary since the strength of the C−C bond in acetaldehyde may be considerably larger than previously supposed.

On the assumption that there exists a correspondence between the bond strength and the beginning of the diffuse region in the predissociation spectrum, one of us has calculated the bond strength of C−C in acetaldehyde as 93.1 kcal.[2] This value is considerably in excess of that suggested by Rice and Herzfeld,[3] namely, 70 kcal. Since by the use of this latter value they succeeded in obtaining the experimentally observed energy of activation for the over-all reaction assuming a particular mechanism, it follows that the postulated energies of activation of the intermediate reactions may also need revision. Of these intermediate reactions the one postulated as terminating the chain, namely, the recombination of methyl radicals, is one about which perhaps the most has been assumed and the least is known.

Combination of Methyl Radicals

There appears to be good evidence that the combination of two methyl radicals to produce ethane must occur, in the gas phase, as a three-body process. Kimball[4] calculates a mean life for the quasi-molecule resulting from the collision of the two radicals alone of 10^{-12} sec. Kassel,[5] while criticizing the use of classical theory in this connection suggests the plausibility at least, that the introduction of quantum restrictions would favor the dissociated state, thus making the classically calculated mean life longer than that based on quantum theory. It will henceforth be assumed therefore, that the reaction should be written:

$$2CH_3+M\rightarrow C_2H_6+M. \qquad (6)$$

The question of the energy of activation remains. Various estimates of this latter have been made, based on little or no direct evidence but rather on intuition. Thus Bawn[6] attempting to calculate steric factors for several reactions by the transition state method remarks "it is also assumed that the reverse reaction ($2CH_3\rightarrow C_2H_6$) requires an activation energy of either zero or 8000 cal." This reference is frequently quoted as the basis for a low energy of activation.

It appears, however, that a reasonably reliable value can be arrived at from our analysis of the acetaldehyde decomposition. The Rice-Herzfeld mechanism with some slight modifications is assumed giving the following scheme:

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

[1] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 414 (1939).

[2] M. Burton, J. Chem. Phys. **6**, 818 (1938).

[3] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 288 (1934).

[4] G. E. Kimball, J. Chem. Phys. **5**, 310 (1937). F. Patat, Zeits. f. physik Chemie **32**, 288 (1936), attempts to calculate the velocity of the three-body combinations using a mean life for the quasi-molecule of 8×10^{-13}. The constant is assumed proportional to absolute temperature.

[5] L. S. Kassel, J. Chem. Phys. **5**, 922 (1937).

[6] C. E. H. Bawn, Trans. Faraday Soc. **31**, 1542 (1935).

$$CH_3CHO \rightleftarrows CH_3 + CHO, \quad (1)$$

$$HCO \rightleftarrows H + CO, \quad (2)$$

$$H + CH_3CHO \rightleftarrows H_2 + CH_2CHO, \quad (3)$$

$$CH_2CHO \rightleftarrows CH_3 + CO, \quad (4)$$

$$CH_3 + CH_3CHO \rightleftarrows CH_4 + CH_2CHO, \quad (5)$$

$$2CH_3 + M \rightleftarrows C_2H_6 + M. \quad (6)$$

It may be remarked in passing, that reaction (2) at least, if not others also in the above scheme, would most probably involve a second body M. Taking M as acetaldehyde, however, the final reaction rate expression is not thereby changed. The postulated scheme differs from the Rice-Herzfeld one in taking $CH_2 \cdot CHO$ rather than $CH_3 \cdot CO$ as the intermediate chain carrier. The strength of the C−H bond in the aldehyde group in acetaldehyde has been calculated as 115 kcal.[2] which would make the removal of the H atom a difficult step. The value for formaldehyde is some 12 kcal. less. Now, Akeroyd and Norrish[7] by photochemical methods have deduced the energies of activation of the reactions:

$$CH_3 + CH_3 \cdot CHO \rightarrow CH_4 + CH_3 \cdot CO$$

and

$$H + H \cdot CHO \rightarrow H_2 + H \cdot CO$$

as 9.8 and 16.2 kcal., respectively, the formaldehyde being the more difficult to break down. This discrepancy disappears if the reactions involve a different hydrogen atom and if the product from acetaldehyde is the radical $CH_2 \cdot CHO$.

Using the customary steady-state method, the observed velocity of acetaldehyde decomposition is deduced from the above scheme as $k_5(k_1/k_6)^{\frac{1}{2}} \times (CH_3CHO)^{\frac{1}{2}}$. The experimental value of the energy of activation is 45.5 kcal. whence

$$45.5 = E_5 + \tfrac{1}{2}(E_1 - E_6).$$

Taking Norrish's value of 10 kcal. for E_5, the quoted bond strength of 93 as a minimum value for E_1, gives $E_6 = 22$ kcal. It should be noted that the value of 15 kcal. used by Rice and Herzfeld for E_5 is not based on any experimental evidence but is assigned to show "agreement with the free radical mechanism."[8]

[7] E. I. Akeroyd and R. G. W. Norrish, J. Chem. Soc. 890 (1936).
[8] F. O. Rice, J. Am. Chem. Soc. **56**, 488 (1934).

Rupture of a Central Molecule

The value of 22 kcal. thus calculated assumes the acetaldehyde molecule as the third body. It seems to be questionable whether the identity of the third body can affect the energy of activation or simply affects the steric factor by a favorable or unfavorable orientation. In discussing this problem with specific reference to the combination of hydrogen atoms, Eyring[9] points out that the ability to transfer energy is intimately connected with reactivity and shows that the marked efficiency of hydrogen as a third body may be caused by its readiness to form a complex with the reacting substances, since, because of its small moment of inertia it is in a favorable configuration about half the time at room temperature. This would appear to emphasize the steric factor rather than the energy of activation so that one might expect an energy of activation of about 22 kcal. for the combination of methyl radicals regardless of the third body.

When, however, the third body is capable of producing an alternative reaction this value of 22 kcal. is not necessarily to be expected. The combination of two hydrogen atoms with a hydrogen molecule as the third body has been shown by Eyring[9] to involve the four atoms in line, reaction occurring when the central molecule splits forming two new hydrogen molecules; a chemical reaction rather than an energy transfer at collision. Such a view effectively interprets a number of observations. Thus, Smith and Kistiakowsky[10] consider the effect of oxygen and hydrogen molecules as third bodies in the reaction between oxygen atoms and oxygen molecules in the photochemical hydrogen-oxygen reaction to be represented as follows:

$$O + O_2 + O_2 \rightarrow O_2 + O_3$$

and

$$O + H_2 + O_2 \rightarrow OH + HO_2$$

where reactants are here written in the order of their linear arrangement on collision and, subsequent to the splitting of the central molecule, the products produced therefrom in the same order.

[9] Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 795 (1935).
[10] H. A. Smith and G. B. Kistiakowsky, J. Am. Chem. Soc. **57**, 835 (1935).

Again, Schumacher and Wolff,[11] in the photochemical chlorination of chloroform have postulated as the chain ending reaction:

$$CCl_3+Cl_2+CCl_3\rightarrow 2CCl_4,$$

where again the linear arrangement of reactants is indicated, showing the probability of rupture of the central molecule as the mechanism and lending credence to the supposed small energy of activation.

Methyl Radicals and Hydrogen

It seems logical to suppose a similar possibility to hold in the combination of two methyl radicals with hydrogen as the third body, namely, the molecule in line with and between the carbon atoms of the radicals. The result of the splitting of the hydrogen molecule would be the production of two methane molecules. Now this is precisely the result that is always observed in systems containing methyl radicals, which, in the absence of hydrogen, yield ethane as the major product but, in presence of hydrogen, show a markedly decreased ethane and increased methane formation. Attention was first called to this result by von Hartel and Polanyi[12] in their investigation of the reactions between sodium vapor and methyl chloride using hydrogen as the carrier gas. They observed methane formation and assumed its production by the reaction

$$CH_3+H_2\rightarrow CH_4+H.$$

The sole evidence for this reaction appears to have been the observation of a *D*-line emission, particularly strong when the reaction zone was heated, which phenomenon they associated with the presence of hydrogen atoms. Since the reaction postulated above:

$$2CH_3+H_2\rightarrow 2CH_4$$

would be highly exothermal (about 87 kcal.), the observed luminescence could easily be accounted for (the *D* line requiring about 48 kcal.), particularly at higher temperatures as observed.

Cunningham and H. S. Taylor[13] have recently offered evidence for the production of hydrogen atoms by methyl radicals and hydrogen in the photolysis of mercury dimethyl in presence of hydrogen. They observed a greater over-all decomposition of the mercury alkyl when hydrogen was present than in its absence. They ascribe this to reaction of the hydrogen atoms, produced from methyl radicals and molecular hydrogen, with the metal alkyl in a chain process:

$$H+Hg(CH_3)_2\rightarrow CH_4+Hg+CH_3.$$

Leighton and Mortensen,[14] however, in studying the analogous decomposition of lead tetramethyl have pointed out that the observed quantum yield of 1.11 in the vapor phase may be a compensated result of longer chains and a considerable recombination of metal with alkyl radicals. That the quantum yield is reduced to unity by oxygen[14] or by nitric oxide[15] merely indicates that the removal of methyl radicals by combination with oxygen or nitric oxide reduces their recombination with metal atoms as well as the chain length. Cunningham and Taylor have not considered the possibility of this recombination to form mercury dimethyl and it appears that in presence of relatively large amounts of hydrogen the recombination would be considerably reduced, giving the appearance of an increased yield. The evidence for hydrogen atoms is again therefore not unequivocal. More especially is this so since Taylor and Rosenblum[16] in a parallel investigation using acetone, do not consider that the hydrogen atoms partake further in the reaction.

In an investigation of the effect of foreign gases on azomethane decomposition Sickman and Rice[17] observed that hydrogen is not an "inert gas" while deuterium is. They conclude that this is because of a difference in reactivity between methyl and hydrogen on the one hand, and methyl and deuterium on the other. They presume reaction to occur in the former case yielding hydrogen atoms which react further

[11] H. J. Schumacher and K. Wolff, Zeits. f. physik. Chemie **B25**, 161 (1934); **B26**, 453 (1934).
[12] H. von Hartel and M. Polanyi, Zeits. f. physik. Chemie **B11**, 97 (1930).
[13] J. P. Cunningham and H. S. Taylor, J. Chem. Phys. **6**, 359 (1938).
[14] P. A. Leighton and R. A. Mortensen, J. Am. Chem. Soc. **58**, 448 (1936).
[15] J. W. Linnett and H. W. Thompson, Trans. Faraday Soc. **33**, 874 (1937).
[16] H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1937).
[17] D. V. Sickman and O. K. Rice, J. Chem. Phys. **4**, 608 (1936).

with azomethane, while no deuterium atoms result in the second case. Such a discrepancy does not appear plausible.[18] If, however, the reactions occurring were the three-body ones, two methyls and either hydrogen or deuterium, then since deuterium has twice the moment of inertia of hydrogen it would be in a favorable configuration for reaction much less frequently than hydrogen and show, consequently, a reduced reactivity.

Perhaps the most convincing evidence for the production of hydrogen atoms from methyl radicals and molecular hydrogen is to be found in the observations by Patat and by Sachsse[19] of a rate of para- to orthohydrogen conversion in systems containing methyl radicals which is higher than that to be expected from the equilibrium concentration of hydrogen atoms at the temperature of the experiments. On the assumption that methyl radicals produce hydrogen atoms by reaction with hydrogen, they have measured the radical concentration in numerous organic pyrolyses. It is extremely significant that they find in all cases a radical concentration that is much smaller than that to be expected on the basis of current theory. It is surprising that the possibility of a disappearance of methyl radicals other than by a reaction producing hydrogen atoms has not been seriously considered.

For comparison with these investigations the work of West[20] offers significant information. In an attempt to determine the paramagnetism of free methyl West studied the *para-ortho* conversion brought about in an illuminated system containing methyl iodide. A small but definite conversion was found. Patat has criticized the suggestion by West that the conversion is due to the paramagnetic effect similar to that found with oxygen and nitric oxide. Applying the Wigner formula he calculates the concentration of methyl that would have been necessary to produce West's observed effect and finds an impossibly high value and concludes that the observed effect, as in his work, must be due to hydrogen atoms. Realizing that the Wigner formula is only an approximation, and that the efficiency of conversion increases as the square of the magnetic moment and with about the sixth power of the distance of closest approach, it is not unlikely that a result, calculated with oxygen as an analogous substance, would be greatly in error. Thus, the distance of approach of a free methyl to a hydrogen molecule might very well be much smaller than for oxygen. An independent method of estimating the conversion efficiency would therefore be useful.[21]

West has shown[22] that the recombination of methyl radicals and iodine atoms, although the fastest secondary reaction in the photolysis, occurs almost entirely on the walls. Using the Einstein-Smoluchowski relation, the number of collisions a methyl radical makes with hydrogen on its way to the wall can be calculated. Knowing the distribution of iodine in the photolytic products, a measurement of the free iodine together with the over-all quantum yield gives the rate of production of methyl radicals. The product of the number of collisions with hydrogen made by each methyl radical and the number of methyl radicals produced in unit time gives the total number of hydrogen molecules that have been influenced by methyl radicals in unit time. Then, from the observed *para-ortho* conversion the collision efficiency of methyl can be estimated. Taking the most unfavorable conditions, the collision efficiency in West's experiments is calculated to be of the order of 10^{-11}. This is about a hundred times greater than that of oxygen; a not impossible eventuality.

There follows, however, an important result. Since the hydrogen atom is approximately 10^6 times as efficient for spin-isomerization as oxygen, and the methyl one hundred times as efficient, if the observed effect is not due to a paramagnetism but as Patat claims solely to hydrogen atoms, then, only one methyl out of 10^4 need produce a hydrogen atom for the given conversion. If the observed *para-ortho* conversion is partly due to the methyl radical itself, this value of 1 in 10^4 would be a maximum. The

[18] Cf., however, E. W. R. Steacie, Chem. Rev. **22**, 329 (1938).

[19] F. Patat and H. Sachsse, Zeits. f. physik Chemie **B31**, 105 (1935); H. Sachsse, *ibid.* **B31**, 79 (1935); F. Patat, *ibid.* **B32**, 274, 294 (1936).

[20] W. West, J. Am. Chem. Soc. **57**, 1931 (1935).

[21] The authors are indebted to Professor West for the analysis in the following paragraph

[22] W. West and L. Schlessinger, J. Am. Chem. Soc. **60**, 961 (1938).

remaining methyls could recombine, or more probably, react by the three-body process with hydrogen, to yield methane.

Numerous attempts have been made to measure the energy of activation of methane production by free methyls in the presence of hydrogen. They have all been interpreted as pertaining to the bimolecular, hydrogen atom producing reaction. Thus von Hartel and Polanyi estimated a value of 8 kcal. Patat, from acetaldehyde photolysis, calculates a maximum value of 9 kcal. using a steric factor 10^{-4}. H. S. Taylor and Cunningham, from mercury dimethyl decomposition, find values lying between 6.6 and 8.1, while from the acetone photolysis values between 8.7 and 11 kcal. are found. They conclude "that the most trustworthy value now available" is 9 ± 2 kcal.

From the above it seems most likely that this is the energy of activation of the three-body reaction:

$$2CH_3+H_2\rightarrow 2CH_4$$

and not of

$$CH_3+H_2\rightarrow CH_4+H.$$

Taking the rate of the former reaction as approximately $10^6\ e^{-E/RT}$ where $E=9\pm2$ kcal. and accepting tentatively that the second reaction occurs at 10^{-4} of the former rate, the rate of the second reaction is given by $10^9\ e^{-E/RT}$ where $E=19\pm2$ kcal. It is indeed surprising that Patat found it necessary in order to explain his experimental results to postulate a steric factor of 10^{-4} for the hydrogen atom producing reaction and thence obtained the energy of activation of 9 kcal. Had the steric factor been taken as unity the value becomes 20 kcal.

Discussion

H. Austin Taylor, *New York University:* The evaluation of E_6 as 22 kcal. is based on the assumption that E_5 has the value 10 kcal. suggested by Akeroyd and Norrish. Since the paper to be presented later by Rollefson and Grahame shows that the energy of activation actually measured in such work is a complex quantity dependent, for example, on the wave-length used, it does not seem justifiable to accept Norrish's value. One can consider an alternative point of view. Equating the observed energy of activation of the thermal decomposition with the energies of activation of the steps in the Rice-Herzfeld scheme gives

$$45.5=E_5+\tfrac{1}{2}(E_1-E_6).$$

Taking E_1 as 93 kcal. yields

$$E_5-\tfrac{1}{2}E_6=-1.$$

The chain length in the decomposition of acetaldehyde promoted by methyl radicals should thus show a small decrease with increase in temperature. This is a result reported by Allen and Sickman in the azomethane promoted reaction, though they offered an alternative explanation.

In connection with the postulated reaction between two methyls and hydrogen the suggestion by Eyring of the existence of the complex CH_3-H-H seems to offer a bimolecular mechanism in two steps to replace the single three-body reaction. Thus:

$$(a)\qquad CH_3+H_2\rightarrow CH_3-H-H$$

$$(b)\qquad CH_3+CH_3-H-H\rightarrow 2CH_4.$$

The over-all result is the same but in either case the implication is inescapable that the 9 kcal. measured is not the energy of activation of CH_3+H_2 but a more complex quantity. The value of 108 kcal. for the C–H bond in methane is thus without foundation.

Richard A. Ogg, Jr., *Stanford University:* I think it is commonly believed that the carbon-carbon bond strength in ethane and acetaldehyde are comparable.

Milton Burton, *New York University:* Before performing the calculations to which reference is made I was of the opinion that the C–C bond strength in acetaldehyde is the same as the C–C bond strength in ethane and that it was around 72 kcal. The assumption involved in the calculation is discussed elsewhere; it is assumed that the value obtained from certain predissociation spectra for polyatomic molecules is generally

correct. That is merely an assumption; some people say that it is a good one, and some say that it is a bad one. It does lead to a value for C−C in acetaldehyde which is 93 kcal. in contrast with the calculated value of 72 kcal. in ethane.

D. C. Grahame, *University of California:* Akeroyd and Norrish's value of 9.8 kcal. for the energy of activation of the reaction

$$CH_3+CH_3CHO\rightarrow CH_4+CH_3CO \qquad (1)$$

was obtained on the assumption that the energy of activation of the recombination reaction

$$2CH_3\rightarrow C_2H_6 \qquad (2)$$

is very small or equal to zero. In any case, the observed heat of activation in the studies of the photolysis of acetaldehyde will equal $E_1-\frac{1}{2}E_2$ or, in general, the energy of activation of the chain propagating step minus half the energy of activation of the chain terminating step. If one agrees also that the thermal decomposition of acetaldehyde proceeds chiefly through a chain process similar to that of the photochemical process, then the conclusion is inescapable that the observed heat of activation of the thermal decomposition equals $\frac{1}{2}E_3+E_1-\frac{1}{2}E_2$, where E_3 is the energy of activation of the reaction

$$CH_3CHO\rightarrow CH_3+CHO. \qquad (3)$$

Without knowing the value of either E_1 or E_2, one may obtain E_3 directly from the over-all value of activation energies observed experimentally. Thus using our value of 8.0 kcal. for $E_1-\frac{1}{2}E_2$, and the value 45.5 kcal. for $\frac{1}{2}E_3+E_1-\frac{1}{2}E_2$, one calculates directly $E_3=75.0$ kcal. This figure represents a maximum value for the C−C bond strength in acetaldehyde. The only real uncertainty in the calculation is the assumption that the thermal decomposition proceeds chiefly through a free radical mechanism.

A. E. Edwards, *University of Wisconsin:* The carbon-carbon bond strength in acetaldehyde may be considerably larger than in ethane because of an electronic resonance between the keto and the enol structures.

Guenther von Elbe, *Coal Research Laboratory, Carnegie Institute of Technology:* Concerning the radical CH_2CHO, in the photo-oxidation of acetaldehyde the formation of peracetic acid is described by the chain-mechanism

$$CH_3CO\rightarrow CH_3CO(OO)\xrightarrow[]{O_2}\xrightarrow{CH_3CHO} CH_3CO(OOH)+CH_3CO.$$

If CH_2CHO is formed instead of CH_3CO, the peracid formation is difficult to understand unless one assumes a rearrangement of the association complex $CH_2(OO)CHO$.

Milton Burton, *New York University:* I agree that Dr. von Elbe's data are better explained by the formation of CH_3CO than by the formation of CH_2CHO. I expect to present more material on bond strengths in a forthcoming paper.

W. Albert Noyes, Jr., *University of Rochester:* The absorption spectrum of acetone consists of numerous bonds superimposed on what appears to be a continuous absorption. The long wave bands are weak and difficult to observe and below 2950A absorption is so general that measurements become impossible. It is not correct to say categorically that the bands change in width or become diffuse as the wave-length is decreased. They merely become more difficult to observe. Therefore I do not believe that the onset of dissociation or predissociation can be ascertained from the appearance of the spectrum.

Paul C. Cross, *Brown University:* The apparent onset of diffuseness in the absorption spectrum of molecules as complex as acetaldehyde is probably due to the rapid increase in the density of the vibrational energy levels with increasing vibrational energy, and is, in general, in no way related to predissociation. The number of energy levels with n quanta of internal energy in x degrees of freedom is

$$\frac{(n+x-1)!}{n!\,(x-1)!}.$$

Thus with $x=15$ and an average fundamental frequency of 1500 cm^{-1}, one would expect the spacing of the vibrational energy levels at 6000 cm^{-1} to be only about one-two hundredth as large as the average spacing of the fundamental frequencies. Even with allowances for

the restrictions on the intensities by the Franck-Condon rule, this increase in the number of vibrational levels should usually produce so much background at a few thousand wave numbers from the O→O vibrational transition as to make the band system appear continuous. In general, the vibrational structure of *all* band systems of *all* complex molecules will be washed out at from a few hundred to a few thousand wave numbers from the origin of the band system. Exceptions may be found in the case of molecules with a high degree of symmetry.

P. A. Leighton, *Stanford University:* The experimental evidence based on tellurium mirror removal shows that methyl radicals are produced in both acetone and acetaldehyde by wavelengths at least as long as 3180A. Unless these are produced by an induced dissociation, with thermal energy contributing to the process, the energy of the carbon-carbon band in these molecules cannot be greater than about 90 cal.

R. A. Ogg, Jr., *Stanford University:* I wish to call attention to the fact that the line of reasoning presented by the authors would invalidate the very large values proposed by H. S. Taylor and co-workers for dissociation energies of methane and ethane, and would reduce these to somewhere near the previously estimated figures (i.e., some 95 kilocalories for C−H and 75 kilocalories for C−C bonds). Nevertheless, the point of departure in the reasoning uses Burton's figure of 93 kilocalories for the dissociation energy of the carbon-carbon bond in acetaldehyde. Such a large constitutive effect on bond energies appears rather unlikely, and I wish to question seriously the reliability of Burton's estimated figure for acetaldehyde. A large number of cases of predissociation are known in which a similar treatment would yield far too large a dissociation energy. Iodine monochloride, for example, has a dissociation energy of some 45 kilocalories. Nevertheless, the first appearance of predissociation in its absorption spectrum occurs in the ultraviolet—corresponding to a much larger energy. In view of the Frank-Condon principle, it would be remarkable if the beginning of predissociation ever corresponded exactly to the dissociation energy. A dissociation energy of some 75 kilocalories for acetaldehyde is entirely compatable with its spectrum.

H. Gershinowitz, *Shell Oil Company:* While it is true that the energy of dissociation of cyanogen measured by Professor Kistiakowsky and myself still stands as the only instance of the direct determination of the energy of a carbon-carbon linkage, I should not put too much emphasis on the value 77±4 kcal. that we found. The resolving power of the Hilger *E*-1 spectrograph used was not sufficient to show the structure of the CH bond. The intensities of the bands were matched by eye since this method gave better results than could be obtained by the best microdensitometer then available to us. It certainly would be desirable to check our value with an instrument of greater resolving power since the thermal dissociation of cyanogen into CN radicals affords a unique opportunity to measure directly a C−C bond energy. It is my impression that Professor Kistiakowsky is reinvestigating this reaction with a 3-meter grating instrument. One would expect that resonance would make the C−C bond in cyanogen stronger than in aliphatic hydrocarbons. I should be surprised, however, if our experimental figure should be raised as high as 93 kcal. I should think 85 kcal. would be a reasonable maximum.

E. P. Wigner, *Princeton University:* The dissociation of N_2O into N_2 and O has a heat of activation of more than 47 kcal. Therefore, all states of the N_2O spectrum which are below 47 kcal. must be expected to be sharp. On the other hand, the heat of dissociation into N_2 and O is only 39.5 kcal. In this case, one cannot expect a simple connection between bond strength and the beginning of the diffuse region in the predissociation spectrum. All this has a perfectly simple reason: the potential between N_2 and O has a maximum outside of the stable minimum which is higher than its value at infinite separation. I wonder whether one can exclude similar cases in other molecules?

Thomas W. Davis, *New York University:* There is nothing fundamentally strange in a wide range of values for C−C bond strengths in differ-

ent compounds. In hexaphenyl ethane, for example, we are confronted with a bond so weak that it dissociates spontaneously into free radicals. To be sure, such a result may be explained by the nature of the substituent groups and factors of "resonance" but such an explanation is precisely what must be offered in all the cases considered.

M. Burton, *New York University:* In reference to the calculation of bond strengths to which allusion is repeatedly made in this discussion, it would be well to clarify the situation. In a recent paper[23] Professor Rollefson and I showed that in *polyatomic* molecules there is good reason to expect a close (not an exact) correspondence between the sudden onset of diffuseness in rotation lines and the strength of the bond involved in the corresponding photochemical act. As the result of suggestions made by Professor Franck at the Stanford Symposium I decided to try the assumption of an *exact* correspondence, to see what modification of our usual assumptions regarding C−C bond strength in ethane and C−H bond strength in methane would be necessitated thereby. The results of such calculation have been published[24] and, as Professor Ogg points out, are, astonishingly enough, in close agreement with the older accepted values of 72 and 95 kcal., respectively.

However, if this method of calculation is to be accepted we are then confronted with inordinately high values for C−C in acetaldehyde and C−H in formaldehyde.[25] The latter value is based upon a sudden broadening of the rotation lines in HCHO reported by Henri[26] and is, perhaps, the best value. That found for CH_3CHO was improperly attributed in my paper,[24] it is really based on a statement by Henri.[27] The point of these remarks is as follows: If the assumption on which the calculations are based is correct, then the C−H bond strength in HCHO is 103 kcal. and the C−C bond strength has a *minimum* value of 93 kcal., assuming the applicability of Professor Cross's remarks.

The remarks of Professor Noyes and Dr. Von Elbe particularly indicate that this subject is by no means complete and that the absorption spectrum in acetone at least may have to be reconsidered. If, as Professor Noyes suggests, we cannot estimate the beginning of predissociation (of the type here considered) by the onset of diffuseness in a polyatomic molecule then one of two conclusions must be correct: either the bond strengths calculated in such cases must have minimum values; or the results calculated so far have been only in *fortuitously* good agreement with the older accepted values for C_2H_6 and CH_4 and the fundamental assumption of exact correspondence is unsound.

[23] M. Burton and G. K. Rollefson, J. Chem. Phys. **6**, 416 (1938).
[24] M. Burton, J. Chem. Phys. **6**, 818 (1938).
[25] The C−C value found for acetone is not germane to the discussion since it is not involved in the calculation.
[26] V. Henri, *The Structure of Molecules* (P. Debye, Editor, Blackie and Son, Ltd., London, 1932), p. 126.
[27] V. Henri, Trans. Faraday Soc. **25**, 767 (1929).

On the Kinetics of Complex Reactions*

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Chemical kinetics is the chemistry of intermediate compounds. These intermediates can be studied directly only with great difficulty but they can be investigated through kinetic measurements themselves. For example during the induction period in the oxidation of hydrogen sulfide the "active centers" are withdrawn from the reaction vessel passed through a connecting vessel and introduced into a chamber in which the new reaction is just starting. The "active centers," responsible for shortening the induction period, are stable for several hours at room temperature. The formula previously given for a chain reaction proceeding from a single active center is extended here to include reactions with any number of active centers. Complex reactions of various types are treated mathematically and experimental curves are given. Among the types of complex reactions considered are those which involve the mutual inhibiting or promoting action of chains with quadratic rupture.

§1. Present Problems in Chemical Kinetics

IN the early twenties of this century chemical kinetics began to develop at a quite astonishing rate. During this period was developed the theory of chain reactions which plays such an important part in the study of complex reactions, as well as the theory of the activated complex which has so satisfactorily solved the problem of the kinetic analysis of the simpler reactions and of the elementary stages of the more complex reactions. However, in the course of the last two or three years, the development of chemical kinetics has slowed down partly because the workers in this field shrink from the immense difficulties in the way of its further development.

Chemical kinetics should not be treated as a branch of physical chemistry. Chemical kinetics represents an entirely new domain of science equal in scope to the domains embraced by inorganic, organic and physical chemistry taken together. It differs essentially from chemistry in that it deals, not with the properties of stable compounds and their structure, but with the chemical process itself, however, complex it may be. Its relation to chemistry is more or less the same as that of physiology to anatomy.

Every chemical process comprises a number of stages, proceeding by various unstable compounds which heretofore have been left out of account by chemistry because of their lack of stability.

Chemical kinetics might rightly be called the chemistry of intermediate compounds. One of the most important and most difficult problems of chemical kinetics consists in the development of simple and reliable methods of analyzing these intermediate compounds in their different stages of reaction. It is the lack of stability and the extreme difficulties inherent in the existing methods which are responsible for the slowing down of the progress of chemical kinetics.

The study of the intermediate compounds consists mainly in taking samples of the reacting mixtures, cooling them rapidly and then proceeding to their chemical analysis. Many difficulties arise: (1) A great number of the intermediate compounds lack stability at room temperature and cannot be kept for the time required for analysis. (2) The microanalytical methods are rather cumbersome and not sufficiently reliable especially in the case of complex mixtures. (3) In the analysis, all the compounds have to be determined, including the side-products, and we have no criterion for choosing those substances which are responsible for the course of the reaction.

The analysis of intermediates has not been used extensively enough, and new improvements should be developed. Attention might be drawn, in this respect, to some attempts at making use of the polarographic method of Heyrovsky.[1] I wish to give here (Table I) one of the polarograms

* This article was communicated to the symposium on "The Kinetics of Homogeneous Gas Reactions," but was not available in time for publication in the preprints. See page 633.

[1] I. J. Heyrovsky, *Theory and Practice of the Polarographic Method.*

TABLE I.

	C_2H_5OOH	CH_2O	C_3H_6O
The mixture contained	0.00264%	0.0318%	0.00715%
The polarogram yields	0.00264%	0.0292%	0.00697%

obtained at our Institute by Stern and Pollak[2] (Fig. 1).

Professor Sokolik of our Institute and his co-workers are now adapting the method to the analysis of the intermediate products formed during the pre-flame period which are responsible for inflammation and detonation in bombs, tubes and internal-combustion engines.

With the aid of the above method Professors Neumann and Dobrinskaja[3] have investigated the increase in the amount of peroxides and aldehydes during the induction period preceding the formation of a cold flame in mixtures of butane and oxygen. The results obtained at a temperature of 310°C and a pressure of 333 mm Hg are given in Fig. 2. Curve 1 shows the variation of the pressure in the mixture with the time, the moment of the formation of the cold flame being marked by an arrow. A special highly-sensitive membrane manometer did not show any variation of pressure during 32 seconds; however, the polarographic analysis of samples of the gas showed a continuous increase in the amount of aldehydes (curve 2) and of peroxides (curve 3, drawn on a scale 10 times as great as that of curve 2). Plotting the logarithm of the aldehyde concentration, a linear increase with the time is obtained (curve 4). This means that, in accord with the theory, the amount of aldehydes increases as $e^{\phi t}$. The polarographic method can thus be applied when the partial pressure of the aldehyde or the peroxide in the mixture is less than 0.1 mm or 0.01 mm Hg, respectively.

Among the physical methods of analysis we might mention that based on the study of absorption spectra. Quite recently Professor Kondratiew of our Institute was able to detect by this method the presence of CS radicals in the cold flame of carbon disulphide. For the study of the extremely unstable products of the type of radicals one might recommend the method of "line spectra" emitted by the products examined, which has been proposed and developed by Kondratiew, and successfully applied by Kondratiew and Avramenko to the analysis of OH in a "cold" hydrogen flame.

However, for different reasons, the absorption method can be applied only in a limited number of cases. Still more limited in its application is the investigation of complex reactions by means of the heavy hydrogen and oxygen isotopes or the artificial radioactive isotopes, though these methods sometimes lead to quite new and important results. Thus Professor Roginsky, of our Institute, and co-workers have found with the aid of radioactive indicators that the monosolvate exchange proceeds in many cases very slowly. They also investigated the kinetics of this process. Professor Roginsky was also able, by using the same method, to throw more light on the mechanism of the catalysis by aluminium bromide.

The mass-spectrograph method appears also to be suitable for the analysis of the intermediate products. However, our attempts in this respect have proved a failure. Neither the physical nor the chemical methods are thus seen to yield simple and reliable means for the analysis of the intermediate products, though in many cases they prove quite helpful and should be developed.

I believe, however, that in general the more universal methods should not be borrowed from other branches of science, but should be based on the principles of chemical kinetics itself. To illustrate the possibility of such methods, I wish to describe here the results of a few experiments which have been recently undertaken by Emanuel and myself.

In the initial stages of any self-accelerating reaction the amount of the substance having undergone reaction varies with the time accord-

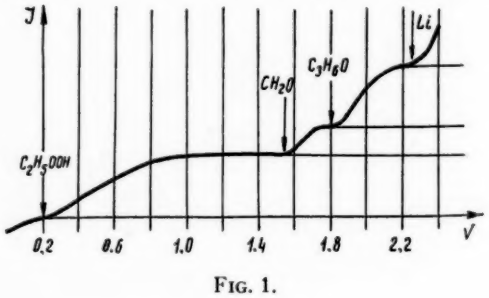


FIG. 1.

[2] Stern and Pollak, Acta Physicochim. 7, 567 (1937).
[3] A. A. Dobrinskaja and M. B. Neumann, Acta Physicochim. 10, 297 (1939). The electrolyte was 1/20 *N* LiCl.

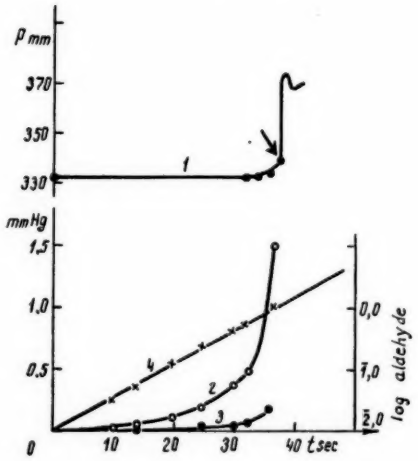


FIG. 2.

ing to the law

$$x = A(e^{\phi t} - 1) \backsimeq A e^{\phi t}.$$

The amount of x can be detected with the aid of an apparatus of a given sensitivity only after a time-interval τ_1 (called "induction period") when it has already attained a definite value x_0. It follows from the theory that the addition of an active product will result in a decrease of this induction period, and it is on this fact that our method has been based.

A mixture of H_2S and O_2 was kept in the vessel 1 (Fig. 3) during a time-interval t_1 (less than the period of induction τ_1 corresponding to the given temperature and pressure) and was then transferred to the vessel 2 maintained at the same temperature. In the vessel 2 the period of induction τ_2 decreases in comparison with its normal value τ_2^0. The experimental relationship between t_1 and τ_2 is shown in Fig. 4. Midway between the vessels 1 and 2 the glass vessel R was placed, kept at room temperature. The mixture, before being admitted to the vessel 2, remained for a certain definite time θ in the vessel R. In our experiments, t_1 was constant and equal to τ_1 (the total induction period). The experimental relationship between θ and τ_2 is shown in Fig. 5. The active centers are seen to be extremely stable at room temperature and to live for several hours.

The relationship between τ_2 and the relative concentration C of the active centers can now be established by diluting the mixture in R which contains a definite number of active centers, with a fresh supply of the mixture, this relationship is shown in Fig. 6. With the aid of the above curve which presents a calibration curve of the given analyzer, we are able to eliminate τ_2 from the curves 4 and 5, and thus answer the following questions: (1) How the relative concentration of the active centers in vessel 1 increases with the time. (2) How the active centers are destroyed in vessel R at room temperature.

The corresponding curves are shown in Fig. 7 and Fig. 8. If log C is plotted instead of the concentration C, fairly straight lines are obtained. This means that (1) in accord with the theory, the accumulation of the active products during the induction period obeys the law $e^{\phi t}$, and (2) that the destruction of the active products at room temperature follows a monomolecular law proceeding in a homogeneous way as established by varying the ratio of surface to volume for vessel R. The above purely kinetic method of analysis, together with chemical and physical methods, will enable us, we hope, to fully investigate the nature of the active products, and not only to find the mass of the product by using, for instance, the diffusion through a small aperture in the membrane, but also to determine its chemical composition and structure by studying its interaction with various reactants in vessel R. Irrespective of the relative value of the method proposed, the possibility of developing new purely kinetical methods for the analysis of the intermediate products is not to be doubted.

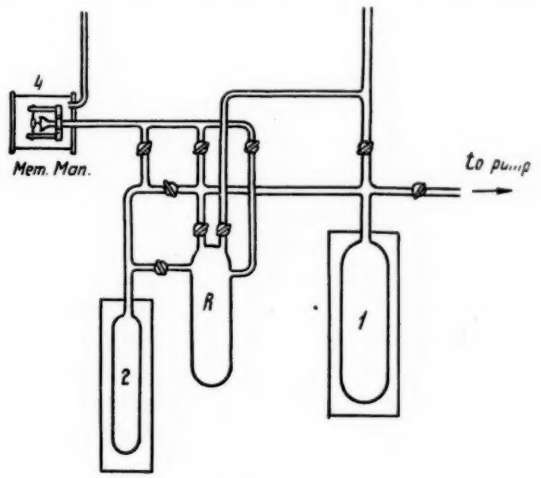


FIG. 3.

The development of reliable methods for the analysis of the intermediate products forms thus one of the main problems of chemical kinetics awaiting solution. But it is not alone the lack of suitable methods which impedes the progress of chemical kinetics. The classification of the chemical reactions according to their formal over-all

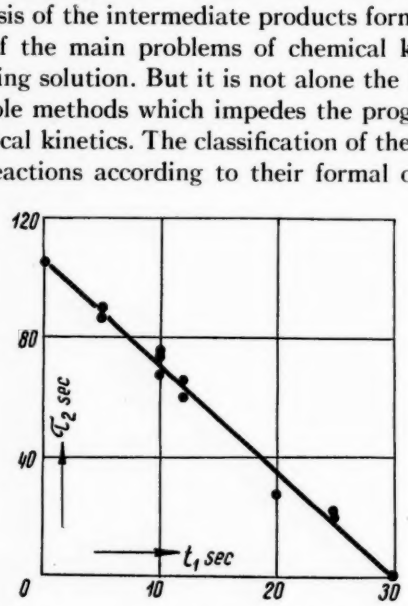


FIG. 4.

kinetics remains one of the main problems of this branch of science, and very little has been done in this respect during the last three years.

As before, research is restricted to a few simple reactions, such as H_2+Cl_2, H_2+O_2, CH_4+O_2 etc., and yet we have no definite knowledge of their kinetics and much less of the mechanism of the reaction. Very often contradictory results are reported by the different authors, and a generalization of the whole experimental and theoretical data available for any of the above mentioned reactions is still lacking. If this state of things persists, it will be long before chemical kinetics obtains the necessary solid foundations for its further development.

It must also be noted that the number of reactions investigated does not widen. It would be timely to proceed to the kinetic investigation of other types of reactions, but we are immediately confronted with several essential difficulties. Thus, for any reaction other than the oxidation processes there have never been observed inflammation limits having the character of chains, at least as far as the upper limit is concerned. It would be hard to believe that the phenomenon is restricted only to oxidation processes. Recently Appin, of our Institute, found characteristics of the upper limit in the inflammation of nitrogen

TABLE II.*

TEMPERATURE °C	p_2 MM HG
20	40
40	70
60	115

* The saturated vapor pressure of NCl_3 at 20°C is 150 mm Hg.

chloride vapor. Above a definite pressure p_2, the vapor did not decompose, appreciably, for many days over a range of temperatures from 0 to 50°; but at pressures below p_2, self-inflammation was observed. The lower limit was either entirely absent or else it lay below 0.01 mm, since even at this pressure the inflammation of the NCl_3 vapor was quite distinct. Table II gives the values of the upper limit p_2 for different temperatures.

Upon the addition of air, the upper limit decreased gradually and, upon a definite dilution, the NCl_3 vapor became practically uninflammable. This appears to indicate that the chain-like inflammation is not limited to oxidation processes alone.

I would like to point out still another circumstance. Some of the workers apparently lack a clear understanding of the fundamental statements of the theory of chain reactions and of the deductions to which it leads. This is sometimes felt when the general laws which, in my book, have been deduced for the case of one single active center are applied to reactions proceeding with a greater number of active centers and also in cases where the rupture and branching are connected with the mutual action of the intermediate products. These two problems were

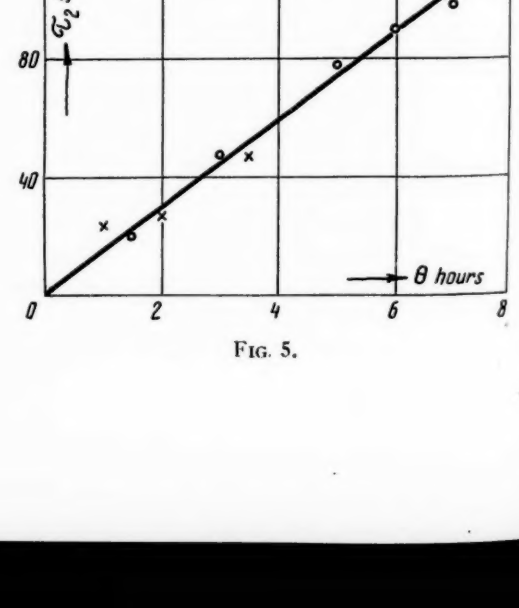


FIG. 5.

not sufficiently elucidated in my book. During the last few years I have developed a complete theory of complex reactions taking into account the disappearance of the initial products by combustion and the self-catalysis by the final products. It should be timely to discuss these problems at the present symposium. Space limitations compel me to restrict myself to the examination of the problems concerning the analysis

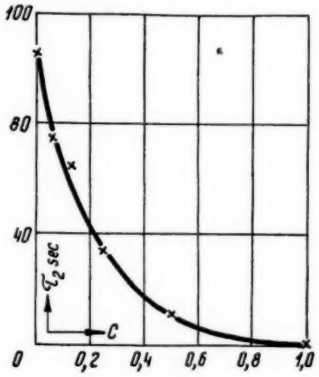


FIG. 6.

of the initial stages of the reaction, leaving aside the more complicated problem of accounting for the disappearance of the initial products by combustion and the self-catalysis by the final products.

§2. Complex Reactions Linear with Respect to the Concentration of the Initial Products

If m different intermediate products participate in the reaction, their respective concentrations n_i will be determined by a system of m differential equations of the type

$$dn_i/dt = n_0^{(i)} + C_{1i}K_1n_1 + C_{2i}K_2n_2 + \cdots + C_iK_in_i + \cdots + C_{mi}K_mn_m, \quad \text{(I)}$$

where $n_0^{(i)}$ is the rate at which the centers n_i are generated spontaneously, at least in one of the above m equations. The term $n_0^{(i)}$ differs from zero. The values of the coefficients C_{ij} are either zero or positive, their order of magnitude being close to 1 or to 2, at the utmost. The values of the coefficients C_i are also positive and always exceed 1.

The above system possesses stationary solutions, proportional to the number n_i^0 of the

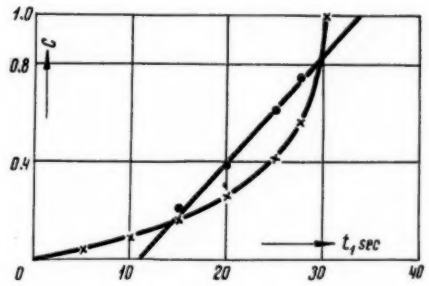


FIG. 7.

centers generated (if one kind of centers is generated), if the determinant D of the homogeneous system satisfies the inequality

$$(-1)^{m+1}D < 0. \quad (1)$$

For $(-1)^{m+1}D > 0$, nonstationary solutions are obtained and the concentrations n_i increase with the time. The solution of the characteristic equation $D(\lambda) = 0$ yields m roots, out of which $(m-1)$ roots are represented either by negative values or by complex quantities with negative real parts. The remaining root $\lambda = \phi$ which, as a rule, is the smallest as regards its absolute value, is either negative, if $(-1)^{m+1}D < 0$, or positive, if $(-1)^{m+1}D > 0$.

This means that for not too small values of t the concentrations of the centers are proportional to $e^{\phi t}$ and therefore to each other. If n_i^0 are the particular solutions of the system (putting $dn_i/dt = 0$), we may expect that to a sufficient degree of precision

$$n_i = |n_i^0|(e^{\phi t} - 1). \quad (3)$$

If $(-1)^{m+1}D < 0$, then it may be expected that

$$n_i = n_i^0(1 - e^{-|\phi| t}), \quad (4)$$

though with a lesser degree of precision (owing

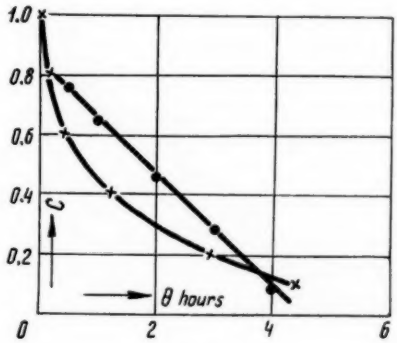


FIG. 8.

to the smaller absolute value of the root $\lambda=\phi$). If $(-1)^{m+1}D<0$, the values of n_i^0 determine those concentrations of the intermediate products which will be established with the time, i.e., the stationary concentrations. The values of n_i^0 are all inversely proportional to $|D|$. The reaction rate which presents a definite linear combination of the values $C_iK_in_i$ is also inversely proportional to $|D|$. If certain conditions are satisfied concerning the order of magnitude of the different K_i, then the value of the smallest root ϕ will also be approximately porportional to D.

The determinant $(-1)^{m+1}D$ can always be represented in the form of some quantity proportional to the difference $\delta-\beta$ (the probability of branching minus that of rupture). Thus the stationary reaction rate $w=Cn_0/(\beta-\delta)$. The nonstationary reaction rate as a function of the time is

$$w=\frac{n_0}{\delta-\beta}(e^{\phi t}-1). \tag{5}$$

In many cases presenting some interest from a practical point of view, $\phi C(\delta-\beta)/\tau$, where τ is the time during which the slowest link develops, C being a positive integer.

For any complex reaction, the condition for the transition from a stationary to a nonstationary régime reads $\delta-\beta=0$. In a number of cases (but not all) δ and β are simple functions of the temperature.

Thus it can be said that all the expressions obtained earlier[4] for the simplest case of a chain reaction proceeding with the aid of one single active center will also hold more or less accurately in the case of reactions with any arbitrary number of active centers.

Example 1

Monocyclic system with three centers.—

$$\begin{aligned}
dn_1/dt&=n_0-(K_1+K_1')n_1\\
&\quad+LK_3n_3=n_0-A_1K_1n_1+LK_3n_3,\\
dn_2/dt&=K_1n_1-(K_2+K_2')n_2=K_1n_1-A_2K_2n_2,\\
dn_3/dt&=K_2n_2-(K_3+K_3')n_3=K_2n_2-A_3K_3n_3.
\end{aligned} \tag{II}$$

Here $K_1'n_1$, $K_2'n_2$, $K_3'n_3$ are the rates at which the chains are broken.

[4] N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935), Part. I.

The value of L can be equal either to zero (complex reaction without chains), or to 1 (simple chain reaction), or to 2 (branching chain). A_1, A_2, A_3 are always greater than 1.

$$(-1)^{z+1}D=D=K_1K_2K_3\Delta,$$

where

$$\Delta=\begin{vmatrix} -A & 0 & L \\ 1 & -A_2 & 0 \\ 0 & 1 & -A_3 \end{vmatrix}=L-A_1A_2A_3. \tag{6}$$

For $D<0$, the stationary solutions are

$$\begin{aligned}
n_1^0&=\frac{n_0}{A_1K_1}\frac{A_1A_2A_3}{A_1A_2A_3-L};\\
n_2^0&=\frac{n_0}{A_1A_2K_2}\frac{A_1A_2A_3}{A_1A_2A_3-L},\quad \text{etc.,}
\end{aligned} \tag{7}$$

the nonstationary solutions, for $D>0$, being

$$n_1=\frac{n_0}{A_1K_1}\frac{A_1A_2A_3}{L-A_1A_2A_3}e^{\phi t}, \tag{8}$$

the reaction rate being

$$w=A_1K_1n_1+A_2K_2n_2+A_3K_3n_3.$$

$1/A_1=\alpha_1$ is the probability that the chain will continue at the first link, $1/A_2=\alpha_2$ the probability that it will continue at the second, $1/A_3=\alpha_3$, at the third link, while $1/A_1A_2A_3=\alpha_1\alpha_2\alpha_3=\alpha$ is the probability that the chain will be continued after a complete cycle. If $L=1$, then $(A_1A_2A_3-1)/A_1A_2A_3=1-\alpha=\beta$ is the probability of a rupture after a complete cycle. Hence $w\backsimeq n_0/\beta$. Since Δ is always <1, any nonstationary solutions are excluded.

For $L=2$, $(A_1A_2A_3-2)/A_1A_2A_3=\beta-\alpha$, and since in the case of a continuously branching chain $\alpha=\delta$, the quantity $\beta-\alpha$ will be equal to $\beta-\delta$. In this case nonstationary solutions are also possible, considering that $L-A_1A_2A_3$ can be >0.

It is easily seen that, if $A_1K_1\ll A_2K_2$ and $\ll A_3K_3$, then

$$\phi=\frac{A_1K_1(2-A_1A_2A_3)}{A_1A_2A_3}=\frac{\delta-\beta}{\tau}, \tag{9}$$

where $\tau=1/A_1K_1$, is the time during which the slowest link develops, being approximately the time during which the complete cycle develops,

since $1/A_1K_1 \gg 1/A_2K_2$, and $1/A_3K_3$. Hence

$$n_1 = \frac{n_0\tau}{\delta-\beta}(e^{(\delta-\beta/\tau)t}-1).$$

It must be noted that this approximate solution corresponds to that which is obtained in system I when putting $dn_2/dt = dn_3/dt = 0$. This approximate method of solution will be satisfactory if $A_1K_1 \ll A_2K_2$ and A_3K_3.

The general aspect of the determinant of this or another complex reaction shows at once the most convenient form of diagram by which to illustrate the system. The above scheme is best represented as in Fig. 9, the diagram being self-explanatory.

Example 2

Bicyclic system with three centers.—A number of schemes of this type are shown in Figs. 10, 11 and 12, all three leading to similar results from a kinetical point of view.

Let us examine the scheme 10, Its equations are:

$$\begin{aligned} dn_1/dt &= n_0 - A_1K_1n_1 + K_2n_2 + K_3n_3, \\ dn_2/dt &= K_1n_1 - A_2K_2n_2, \\ dn_3/dt &= K_2n_2 - A_3K_3n_3. \end{aligned} \qquad \text{(III)}$$

The determinant

$$D = K_1K_2K_3\Delta,$$

where

$$\Delta = \begin{vmatrix} -A_1 & 1 & 1 \\ 1 & -A_2 & 0 \\ 0 & 1 & -A_3 \end{vmatrix} = 1 - A_3(A_1A_2 - 1). \qquad (10)$$

Let us denote by D_1 the minor of the determinant D. Then $D_1 = K_1K_2\Delta_1$; $\Delta_1 = A_1A_2 - 1$. This minor corresponds to the determinant of the chain reaction of the first cycle alone of the given bicyclic system (10). The precise solution of the above system of equations yields the following rule for obtaining an approximate expression for the value of ϕ in the expressions $n_i = n_i^0(e^{\phi t} - 1)$ determining the variation of the concentration n_i with the time in the case of a nonstationary régime ($D > 0$).

(a) If $A_2K_2 \gg A_1K_1$ and A_3K_3, and

$$DA_2K_2/D_1^2 \ll 1, \qquad (11)$$

then we may put $dn_1/dt = dn_2/dt = 0$ in solving the system (III). At the same time

$$\phi = K_3\Delta/\Delta_1. \qquad (12)$$

(b) If $A_2K_2 > A_1K_1$ and A_3K_3 and

$$D/A_2K_2(A_3K_3)^2 \ll f, \qquad (13)$$

then in solving the system (III) we may put $dn_2/dt = dn_3/dt = 0$. At the same time

$$\phi = K_1\Delta/A_2A_3. \qquad (14)$$

For $D < 0$, the stationary solutions are:

$$n_3^0 = \frac{n_0}{A_1A_2A_3K_3}\frac{A_1A_2A_3}{A_3(A_1A_2-1)-1}, \text{ etc.} \qquad (15)$$

If the first cycle of the bicyclic system be looked upon as the fundamental chain, then $1 - 1/A_1A_2 = \beta$ is the probability of rupture. The probability of the continuation of the second cycle $\alpha = 1/A_1A_2A_3$ will at the same time represent the probability of branching with respect to the fundamental chain. Hence

$$\frac{A_1A_2A_3}{A_3(A_1A_2-1)-1} = \frac{1}{\beta-\delta}.$$

The stationary reaction rate $w = C(n_0/\beta - \delta)$ where C is of the order of 1.

In the case of a nonstationary reaction

$$w = C\frac{n_0}{\delta-\beta}(e^{\phi t}-1).$$

If the fundamental chain is sufficiently long and the branchings few, then $K_1' \ll K_1$, $K_2' \ll K_2$, $K_3 \ll K_3'$. Hence

$$\delta = \frac{1}{A_1A_2A_3}\frac{K_3}{K_3'} \quad \text{and} \quad \beta = 1 - \frac{1}{A_1A_2}\backsimeq\frac{K_1'}{K_1} + \frac{K_2'}{K_2}.$$

Since all the values K are temperature functions of the type $e^{-E/RT}$, it follows that one of the ratios K_1'/K_1 and K_2'/K_2 will be considerably greater than the other. Thus in the case of long chains with few branches β and δ are simple temperature functions of the type $e^{-E/RT}$.

The value of ϕ in expression (11) is equal to

$$\phi = \frac{K_3\Delta}{\Delta_1} = \frac{A_3K_3(\delta-\beta)}{\beta} = \frac{\delta\gamma - 1}{\theta}, \qquad (16)$$

where γ is the length of the fundamental chain, and θ, the time required for the branching, is great in comparison with the time required for the development of the fundamental chain, since the condition (11) will be satisfied only if

$$DA_2K_2/D_1^2=K_3\Delta A_2/K_1\Delta_1^2\ll 1.$$

Thus we are dealing with a case of "degenerate branching," as it has been called in my book.

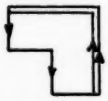


FIG. 9.

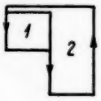


FIG. 10.

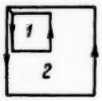


FIG. 11.

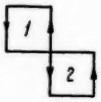


FIG. 12.

It can be easily seen that expression (16) is identical with that given in my book.

In case (b) according to (14)

$$\phi=\frac{K_1\Delta}{A_2A_3}=\frac{A_1K_1\Delta}{A_1A_2A_3}=\frac{\delta-\beta}{\tau},$$

where τ is the time required for the development of the first cycle (since $1/A_1K_1\gg 1/A_2K_2$). Thus a formula is obtained similar to that given in my book for chains where the branching does not proceed more slowly than the development of the fundamental chain.

The following conclusions can thus be drawn.

(1) For any complex reaction, the transition of the stationary to the nonstationary state is determined by the condition $D=0$ which is equivalent to $\beta-\delta=0$.

(2) In the case of a nonstationary state, however complex the reaction may be, the reaction rate (for values of t that are not too small) is always expressed by a function of the type $e^{\phi t}$, and the concentrations of all the intermediate products are proportional to each other.

(3) In most of the complex reactions presenting some interest from a practical point of view, if the branching does not proceed considerably more slowly than the development of the fundamental chain $\phi=(\delta-\beta)/\tau$, while in the case of degenerate branching $\phi=(\delta\gamma-1)/\theta$.

(4) For long chains with few branchings, β and δ are simple functions of the temperature of the type $e^{-E/RT}$.

(5) In the case of schemes that are not too complex—having but two or three kinds of centers—the reaction is best characterized by the values of β and δ. In the case of still more complex schemes, the values A and L are more appropriate.

§3. Mutual Inhibiting Action of the Chains. Quadratic Rupture

If the rupture of the chains is due not only to the interaction of the active centers with the wall or with the initial products (rupture of the linear type), but if in addition some of the centers perish owing to recombination or to some other kind of mutual action, then the system of equations determining the course of the reaction ceases to be linear. We shall restrict ourselves to the examination of one single case where only one of the centers perishes owing to recombination at a rate Bn_1^2.

(a) Quadratic rupture in a monocyclic system

$$\begin{aligned} dn_1/dt&=n_0-A_1K_1n_1+LK_3n_3-Bn_1^2,\\ dn_2/dt&=K_1n_1-A_2K_2n_2, \qquad (I)\\ dn_1/dt&=K_2n_2-A_3K_3n_3. \end{aligned}$$

For the solution of the above system of equations the same determinant will be of use, as for the purely linear scheme of §2.

$$D=K_1K_2K_3\Delta$$

where $$\Delta=\begin{vmatrix} A_1 & 0 & L\\ 1 & -A_2 & 0\\ 0 & 1 & -A_3 \end{vmatrix}=L-A_1A_2A_3. \quad (1)$$

If $\Delta<0$, the system has a stationary solution, namely,

$$n_1=\frac{2n_0}{(F^2+4Bn_0)^{\frac{1}{2}}+|F|}, \qquad (2)$$

where $F=A_1K_1\Delta/A_1A_2A_3$ is <0, $|F|$ denoting the absolute value of F. For low values of n_0, expression (2) reduces to

$$n_1=\frac{n_0}{|F|}=\frac{n_0}{A_1K_1}\frac{A_1A_2A_3}{|\Delta|}, \qquad (2')$$

this being the same solution as for the system of linear equations.

If $\Delta>0$, the linear system led to an infinitely autoaccelerating reaction, now this increase is

limited by the quadratic term; another stationary solution is thus obtained, independent of n_0 (for low values of n_0) and corresponding to concentrations and velocities much higher than those for $\Delta<0$.

In this case $\Delta>0$ and $F=A_1K_1\Delta/A_1A_2A_3>0$,

$$n_1=\frac{2n_0}{(F^2+4Bn_0)^{\frac{1}{2}}-F}, \tag{3}$$

which, for low values of n_0, yields

$$n_1=\frac{F}{B}=\frac{A_1K_1\Delta}{A_1A_2A_3B} \tag{3'}$$

and the reaction rate

$$w=K_1n_1=A_1K_1^2\Delta/A_1A_2A_3B.$$

If $A_1K_1\ll A_2K_2$ and A_3K_3, the solution of the system can be obtained by putting $dn_2/dt=dn_3/dt=0$, whence

$$dn_1/dt=n_0+Fn_1-Bn_1^2 \tag{II}$$

which for $\Delta>0$ gives

$$n_1=\frac{2n_0(e^{\sqrt{q}\,t}-1)}{(\sqrt{q}+F)+(\sqrt{q}-F)e^{\sqrt{q}\,t}}, \tag{4}$$

where $q=F^2-4Bn_0$.

For small vales of n_0, the above expression reduces to

$$n_1=(n_0/F)(e^{Ft}-1) \tag{5}$$

for low values of t, and to $n_1=F/B$, for high values of t.

Thus, at the beginning of the process until the stationary velocity has been attained, the increase of n_1, and therefore the increase of the reaction rate, obeys the same law as in the case of a linear scheme; in the course of time this increase slows down, leading to a constant concentration F/B and a constant velocity.

Thus, if the stationary reaction rate is so high that the reaction changes to thermal explosion even before this velocity has been attained, then the quadratic rupture can be neglected; it suffices then to examine only the linear scheme, assuming as before, that the condition $A=0$ continues to determine the transition to a non-stationary régime.

Such is the case for rapid reactions (inflammation). Indeed, for a recombination of the type $H+H+M=H_2+M$, the constant B is of the order of $10^{-32}\times10^{18}=10^{-14}$ at pressures of the order of 1/10 of an atmosphere. In order that the reaction rate K_1^2/B be low, of the order of 10^{14} molecules per second, the value of $1/K_1$ must be equal to about one second. For such low developments of the link of the chain and for low values of n_0, the delay of inflammation should be of the order of tenths of a minute, but for the H_2+O_2 reaction this is different. Thus Kowalsky found $1/K_1$ equal to about 1/10th of a second at a pressure of ~1 mm. At a pressure of 100 mm, $1/K_1$ would therefore attain $\sim10^{-3}$ sec. If we put $K_1=10^3$, the reaction rate K_1^2/B becomes $\backsimeq10^6/10^{-14}\backsimeq10^{20}$ molecules per second and is practically infinite.

Thus, when examining the upper and lower limits for rapidly-proceeding reactions of the type H_2+O_2, the quadratic ruptures can be left out of account though they are often present.

(b) Quadratic rupture in polycyclic schemes

Let us examine a scheme of this kind, as illustrated in Fig. 11, but showing in addition a quadratic rupture at the right lower corner.

$$\begin{aligned} dn_1/dt&=n_0-A_1K_1n_1+LK_2n_2+K_3n_3,\\ dn_2/dt&=K_1n_1-A_2K_2n_2,\\ dn_3/dt&=K_2n_2-A_3K_3n_3-Bn_3^2. \end{aligned} \tag{III}$$

The determinant of the linear part of the scheme is

$$\Delta=LA_3+A_2-A_1A_2A_3=A_2-(A_1A_2-L)A_3. \tag{6}$$

The determinant of the first cycle $n_1-n_2-n_1$ is

$$D=K_1K_2K_3\Delta_1 \quad \text{where} \quad \Delta_1=(A_1A_2-L). \tag{7}$$

If $\Delta_1>0$ and $\Delta<0$, the stationary solution, for low values of n_0, is

$$n_3=\frac{n_0}{|\Delta|}\frac{A_1A_2A_3}{A_1A_2}, \tag{8}$$

i.e., the same as for a scheme without quadratic rupture. If $\Delta_1>0$ (occurring only on the condition that $L\geqslant2$) and $\Delta>0$, then, for low values of n_0, the stationary solution becomes

$$n_3=K_3\Delta/B\Delta_1=D/BD_1 \tag{9}$$

and $$w \backsimeq K_1 n_1 = \frac{K_3^2 \Delta A_2}{\Delta_1^2 B} = \frac{K_1 K_2 K_3 D}{B D_1}. \qquad (10)$$

For $\Delta_1 \leqslant 0$ and $\Delta > 0$, the solution becomes nonstationary. A bicyclic system differs from a monocyclic one in this feature and its physical meaning is that, if $\Delta_1 \leqslant 0$, the chain $n_1 - n_2 - n_1$ (i.e., a chain consisting of two links) leads to an infinitely high reaction rate, if all the centers n_3 perish, so that the quadratic rupture does not play any rôle in the process.[5]

If the conditions of § 2, especially (11) and (13), are satisfied, we may put, in scheme (III), $dn_1/dt = dn_2/dt = 0$ and reduce it to the equation

$$\frac{dn_3}{dt} = \frac{n_0 A_2}{\Delta_1} + K_3 \frac{\Delta}{\Delta_1} n_3 - B n_3^2, \qquad (IV)$$

having the same dependence upon the time as (II).

If the stationary reaction rate $w = K_3^2 \Delta A_2 / \Delta_1^2 B$ becomes very considerable already at $\Delta_1 \backsimeq +1$, then the term $B n_3^2$ can be neglected as it was in the monocyclic scheme. However, if the stationary reaction rate is low (this, as already mentioned, will be the case only for slowly developing reactions) then the bicyclic scheme leads to new results, namely that the condition for the transition to a nonstationary régime is no longer $\Delta = 0$, but $\Delta_1 = 0$. This would mean that, in the case of a very pronounced rupture, the condition for inflammation is $\beta - \delta = 0$ for the first cycle $(n_1 - n_2 - n_1)$; while the second cycle, owing to the marked quadratic rupture, ceases to further the development of the reaction.

The above fact is of interest for any question relating to the nature of the explosion accompanying the oxidation of methane, hydrogen sulphide or arsine; as has been shown by Norrish in England and, in our Institute, by Shantarovitch, Jakovlev and Emanuel, these are typical cases of chain reactions with quadratic rupture developing slowly with time.[6]

In all these cases the oxidation proceeds slowly, the velocity first increasing according to the law $(e^{\phi t} - 1)$ and then (when 10–20 percent has been consumed) attaining a constant value, after which it slowly decreases owing to lack of combustibles. Lowering the pressure or diminishing the diameter of the containing vessel leads to conditions where Δ becomes less than 0. Owing to the low value of n_0, the reaction then practically ceases, as has been shown by Norrish for methane, by Spence for acetylene and, very clearly, by Shantarovitch for arsine. The increase of the temperature or the pressure is followed by a gradual acceleration until explosion sets in. The experimental evidence thus far available, points to thermal causes of the explosion (heating due to the normal temperature coefficient of the stationary reaction). However, in some cases, this cause may be sought in the acceleration caused by the decrease of Δ_1 to zero, or to be exact to almost zero. According to this explanation the explosion bears an essentially chain character. Such is the opinion of Bernard Lewis.

It must be noted that the above mechanism requires the condition that $L \gg 2$ and that at least one of the values of A be greater than unity. If $L = 1$, and at least one $A > 1$, then Δ_1 cannot be zero; if all the coefficients $A = 1$ (i.e., in the absence of linear rupture), then Δ_1 is always equal to zero (even if $L = 1$) and the stationary régime becomes impossible. In a recent paper Jost and Müffling[7] give a scheme for hydrogen oxidation where the transition from a finite stationary reaction rate to an infinite one does not require linear ruptures and can proceed with a quadratic rupture alone. As far as I am aware, this idea is quite new, but it has no physical meaning in the case of the rapidly proceeding low temperature inflammation of hydrogen.[8]

This is easily understood. It suffices to modify the scheme slightly, assuming that, upon the reaction of the center n_1, the centers n_2 and n_2 do

[5] The case will be different if, in addition to the quadratic rupture $B n_3^2$, ruptures of the type $C n_1^2$ and $C n_2^2$ must also be considered.

[6] R. G. W. Norrish and S. G. Foord, Proc. Roy. Soc. **A157**, 503 (1936); P. S. Shantarovitch, Acta Phisicochim. U.S.S.R. **7**, 417 (1937); N. Semenoff, Acta Phisicochim. **9**, 453 (1938).

[7] W. Jost and L. v. Müfflng, Zeits. f. physik. Chemie **183**, 43 (1938).

[8] Other statements appear to be open to criticism as for instance the statement that the determinant of a complex linear chain reaction scheme cannot be represented in the form of the difference $\beta - \delta$ (δ being the probability of branching and β that of the chain being broken), or the statement that my fundamental conceptions are contradicted by the presence in the denominator of the expression for the raction rate in schemes with a quadratic rupture of the square of $|\beta - \delta|$. Furthermore, the authors are examining a homogeneous system, where all the n_0 values are equal to zero and they do not consider the physical complications occasioned by neglecting n_0.

not appear simultaneously, either one or the other being produced at a time.[9]

In the system of Eqs. (III), the term K_1n_1 in the second equation will be multiplied by the fraction $a=K_{11}/K_1$, and by the fraction $b=K_{12}/K_1$ in the third equation, where $K_1=K_{11}+K_{12}$ (the sum of the reaction rates characterizing one or the other alternatives). The sum of a and b is equal to unity.

In the diagrams of the schemes these alternatives are shown by dotted lines (the place of the quadratic branching being marked by a cross X). Fig. 13 represents the scheme for $L=2$. Here it is obvious that the reaction of the center n_1 along the second cycle will be equivalent to a linear rupture with respect to the first cycle. And, therefore, in the case of a strong pronounced quadratic rupture which reduces the action of the second cycle to nothing, the stationary reaction will take place even for $A_1=A_2=A_3=1$, and then the transition from a stationary to a nonstationary régime becomes possible.

In this case the determinant

$$\Delta=\begin{vmatrix} -1 & 2 & 1 \\ a & -1 & 0 \\ b & 0 & -1 \end{vmatrix}=b+2a-1=a$$

and the determinant

$$\Delta_1=\begin{vmatrix} -1 & 2 \\ a & -1 \end{vmatrix}=1-2a.$$

Whence, from (9) and (10)

$$n_3=\frac{K_3\Delta}{B\Delta_1}=\frac{K_3a}{B(1-2a)}=\frac{K_3K_{11}}{B(K_{12}-K_{11})},$$

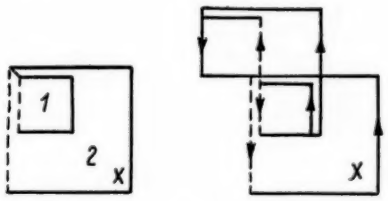
$$K_1n_1=\frac{K_3^2\Delta}{\Delta_1^2B}=\frac{K_3^2a}{B(1-a)}=\frac{K_3^2K_1K_{11}}{B(K_{12}-K_{11})^2},$$

$$K_2n_2=\frac{K_3^2K_{11}^2}{B(K_{12}-K_{11})^2},$$

i.e,

$$w\backsimeq R/(K_{12}-K_{11})^2.$$

Upon a change of the temperature or the pressure, $1-La$ becomes either greater or less than 1, and thus, for $L\geqslant 1$, the transition from a stationary to a nonstationary régime becomes possible in the absence of linear ruptures. The physical meaning of the above is clear only in the case of a very low stationary reaction rate, i.e., when K_3^2/B is small, which, as has already been pointed out, is hardly the case in the oxidation of hydrogen.



FIGS. 13 and 14.

In conclusion let us reproduce Jost's scheme determined by the following chemical equations:

1. $OH+H_2=H_2O+H$,
2. $H+O_2=OH+O$,
3. $H_2+O=OH+H$,
4. $H+O_2+M=HO_2+M$,
5. $2HO_2=H_2O_2+O_2$,
6. $HO_2+H_2=H_2O_2+H$,
7. $H_2O_2+H=H_2O+OH$.

It may be noticed that the last equation is not at all characteristic of the scheme; the same results can be obtained without it, assuming that the H_2O_2 transforms into H_2O according, for instance, to the reaction $2H_2O_2=2H_2O+O_2$. The system of the first six reactions is shown by the diagram of Fig. 14 representing a polycyclic system consisting of a group of linear cycles and of one cycle possessing an alternative bond and containing a quadratic rupture. This system does not differ in principle from the case examined. Indeed, if we write down the determinant Δ together with the determinant Δ_1 of the group of linear cycles, then, with the aid of (9) and (10), we obtain the concentration of the active centers and the reaction rate. The results are of course similar to those obtained by Jost, except that in place of K_4 we get (K_4+K_2), since Jost did not take into account the water produced in the first reaction. If I take the liberty of reproducing these results, it is because expressions (9) and (10), as well as the diagram of the scheme, allow of a more concrete interpretation of the physical meaning of the relations to which schemes of this kind are leading.

[9] Thus, in the reaction $O+H_2=OH+H$, the centers OH and H occur simultaneously. On the other hand, in the reactions $H+O_2+H_2=H_2O+OH$ and $H+O_2+M=HO_2+M$, either the center OH or the center HO_2 arises.

§ 4. Mutual Promoting Action of the Chains. Quadratic Branching

Out of the great number of cases of this kind, we shall examine only one, where the development of the fundamental chain is due to two active centers and the resulting intermediate product n_3 perishes in two different ways: either reacting at a reaction rate $K_4 n_3$ up to a certain final product (perishing without having contributed towards the development of the fundamental chain), or reacting up to another final product the reaction rate being proportional to the square of n_3 ($K_3 n_3^2$), and producing at the same time an active center of the fundamental chain. We shall assume that $K_3 n_3 \ll K_4$ and it is obvious that, throughout the reaction, n_3 cannot become greater than N, the number of molecules of the combustible in the initial mixture.

To illustrate this case let us examine the scheme for the oxidation of carbon disulphide:

1. $CS+O_2=COS+O$ } fundamental chain.
2. $O+CS_2=CS+SO$ }
1′ $CS+CS_2+O_2=(CS)_2+SO_2$ } rupture of chain.
2′ $O+O_2+M=O_3+M$ }
1″ $CS+$wall }
2″ $O+$wall }
3. $SO+SO=SO_2+S$; $S+CS_2=S_2+CS$ (quadratic branching).
4. $SO+O_2=SO_3^*$; $SO_3^*+O_2+CS_2=2SO_2+COS$ (destruction of the intermediate product).

The spontaneous production of the active centers is due to the extremely slow reaction $CS_2+O_2=CS+SO_2$. The resulting COS can be gradually oxidized in an independent way according to the scheme

$$COS+O_2=CO+SO_2.^{10}$$

The constants K_1, K_2, K_3, K_1' etc. are functions of the molecular concentrations of the reactant gases. In the case of the above scheme the corresponding relations are $K_1=\kappa_1(O_2)$; $K_2=\kappa_2(CS_2)$; $K_3=\kappa_3$; $K_4=\kappa_4(O_2)$, $K_1'=\mu(CS_2)(O_2)$; $K_2'=\mu_2(O_2)(M)$.

When the probability ϵ is close to unity, that the active center will perish on striking the wall, then K_1'' and K_2'' are of the same order as D_0/d^2p, while in the case of very low values of ϵ, they will be of the same order as $\epsilon u/4d$. In these relations d is the diameter of the containing vessel, u the velocity of the center due to thermal motion, D_0 the coefficient of diffusion at $p=1$ mm, p the total pressure, $\kappa_{1,2,3,4}$ the constants of the bimolecular, and $\mu_{1,2}$ that of the trimolecular reaction. If the development of the fundamental chain, its branching and the destruction of the intermediate products proceed by bimolecular reactions, and the rupture of the chains in the volume proceed by a trimolecular reaction, then, irrespective of the chemical mechanism of the process, we may assume that K_1, K_2 and K_4 are proportional to p, and that K_1' and K_2' are proportional to p^2, K_3 being independent of the pressure. With regard to K_1'' and K_2'', they may be assumed either to be independent of, or inversely proportional to p (according to the particular value of ϵ).

The corresponding equations have the form

$$dn_1/dt=n_0-A_1K_1n_1+LK_2n_2+K_3n_3^2,$$
$$dn_2/dt=K_1n_1-A_2K_2n_2,$$
$$dn_3/dt=K_2n_2-K_4n_3-K_3n_3^2,$$

where

$$A_1=\frac{K_1+K_1'+K_1''}{K_1};\quad A_2=\frac{K_2+K_2'+K_2''}{K_2},$$

the determinant of the fundamental chain being $\Delta_1=A_1A_2-L$; let us denote by Δ, the quantity $1+L-A_1A_2$.

In all cases concerned, Δ and Δ_1 are >0. If $\Delta_1 \leqslant 0$, we are dealing with a nonstationary reaction, even in the absence of quadratic branching.

Let us first examine the stationary solutions. We have

$$K_1n_1=n_0+K_3n_3^2/(\Delta_1/A_2) \qquad (1)$$

and

$$n_3=\frac{n_0}{K_4\Delta_1}\cdot\frac{2}{1\pm(1-\rho)^{\frac{1}{2}}}, \qquad (2)$$

[10] Professor Kondratiew of our Institute, when studying the cold-flame oxidation of CS_2 by the method of absorption spectra, showed that large amounts of CS radicals and SO molecules are formed in the course of reaction. The amount of CS radicals exceeds by many times the equilibrium concentration at the given temperature. The CS radicals possess a lifetime of several minutes at room temperature and do not react noticeably with the oxygen. The latter fact gives rise to some doubt as to whether the CS radicals can be centers of the fundamental chain. This will be clear only after the examination of their interaction with oxygen at temperatures of the order of 100°C. The final products consist of CO, SO_2 and a considerable amount of COS. Kondratiew's paper has just gone to press.

where $$\rho=\frac{4n_0K_3\Delta}{K_4^2\Delta_1^2} \qquad (3)$$

For low values of n_0, the value of ρ is equally low. For very low values of n_0, one of the two roots is

$$(n_3)_1=n_0/K_4\Delta_1, \qquad (4)$$

the corresponding reaction rate (proportional to K_1n_1 or to K_4n_3) being n_0/Δ_1. This solution does not differ from that which would be obtained in the absence of quadratic branching. This is the required root. The second root

$$(n_3)_2=\Delta_1K_4/K_3\Delta, \qquad (5)$$

having an entirely different physical meaning, will be discussed later.

Thus, in order to obtain a stationary solution, in (2) the sign + should be taken. Upon the decrease of Δ_1, or the increase of n_0, the value of ρ increases, until it can be no longer neglected in (2). In this case the concentrations n_1, n_2 and n_3 and the corresponding reaction rates K_1n_1 and K_4n_3 do not increase in the same proportion as n_0 (at a given Δ_1) but more rapidly. This appears to be the case in the photochemical reaction H_2+Cl_2, with intense illumination (Kokotschaschwili). Recent and more detailed unpublished investigations of Lavrov and coworkers (Leningrad) show that since the increase of the reaction rate with the light intensity I (in the case of intense illumination) is greater than that required by the law of proportionality, the reaction cannot be explained by the heating of the mixture and in fact it takes place even under isothermal conditions. There is some reason to believe that we are dealing here with a mutual promoting action of the chains.[11]

Upon a further increase of ρ, at the expense of the increase of n_0 or of the increase of temperature, resulting in a decrease of Δ_1, a value greater than 1 can be obtained. The expression under the radical sign in (2) acquires an imaginary value, a stationary solution being impossible. From $\rho=1$ upwards, the reaction accelerates with time. In the absence of quadratic branching, the condition for the transition to a nonstationary régime (the condition for inflammation) would be

$$\Delta_1=0. \qquad (6)$$

If the rupture proceeds in the volume and on the surface according to the above scheme, condition (6) would determine the "peninsula of inflammation" with its upper and lower limits. In the case of a reaction of a linear type, the boundaries of this region are independent of n_0.

Now, if a quadratic branching must also be accounted for, the condition (6) can be replaced by another, namely, $\rho=1$ which according to (3) becomes

$$\Delta_1=(4n_0K_3\Delta)^{\frac{1}{2}}/K_4. \qquad (7)$$

This means that the inflammation proceeds more readily (i.e., the temperature of the inflammation falls) and further that the boundaries of the region of inflammation become dependent on n_0; the peninsula of inflammation shifts towards lower temperatures, if the number of initial centers is increased by some artificial means (illumination). The latter effect is characteristic of the mutual promoting action of the chains but it must be convincingly proved that the effect is not due to a heating of the gas. Experimental evidence appears to show that such is the case for a low temperature reaction of hydrogen inflammation.

At the limit of inflammation, i.e., for $\rho=1$, we have according to (2)

$$n_3^*=2n_0/K_4\Delta_1 \quad \text{and} \quad (K_1n_1^*)\backsimeq w^*=Cn_0/\Delta_1, \qquad (8)$$

where C is of the order of 2.

Thus, in the case of quadratic branching, the maximum value of the stationary concentration and that of the reaction rate only twice exceed the corresponding values characterizing the same process at the same temperature in the absence of quadratic branching. In the latter case, for a great number of oxidation processes of the type of chain reactions, the reaction rate $n_0/\Delta_1=n_0/(\beta-\delta)$ rises very slowly with the temperature, and only close to the self-inflammation limit (where $\beta-\delta$ approaches 0), does this increase become rapid. For these simple linear

[11] It can be assumed that the mechanism of quadratic branching is connected with a reaction between chlorine and the HCl* molecule which is extremely rich in energy and is formed in the reaction $H+Cl_2=HCl^*+Cl$ according to the scheme $HCl^*+Cl_2=H-\overset{Cl}{\underset{Cl}{}}Cl$. A branching process of the following form can be imagined to proceed upon collision of the two not very stable HCl_3 molecules: $HCl_3+HCl_3=2\,HCl+Cl_2+Cl+Cl$.

schemes the quantum yield, equal to $1/\Delta_1$, is low over the whole range of temperatures, except those which are close to the region of self-inflammation. In the case of quadratic branching, for high values of n_0, the region of self-inflammation shifts considerably towards lower temperatures, while the reaction rate and the quantum yield on the boundary of the new region are almost the same as in the absence of quadratic branching, i.e., very low. This is characteristic of this type of reaction.

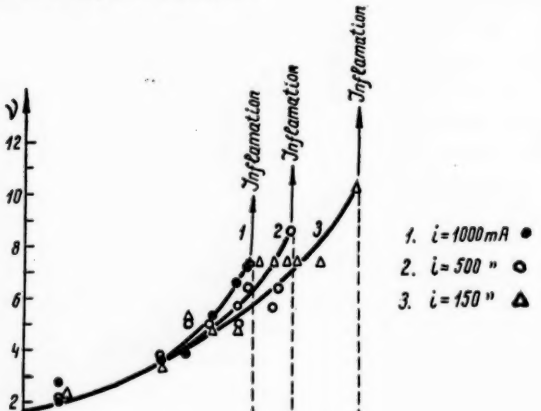


FIG. 15.

The same characteristic features are displayed by hydrogen-oxygen mixtures near the region of low-temperature inflammation, as has first been shown by Dubovitzky[12] and later by Nalbandjan of our Institute. At the very boundary, the length of the chain ν, equal to half of the quantum yield, does not exceed 10. Fig. 15 gives some of the curves obtained by Nalbandjan showing the variation of the quantum yield with the temperature up to the region of inflammation (which depends on n_0). Curve 1 refers to the maximum illumination (in arbitrary units i), curve 2 to a twice fainter illumination, and curve 3 corresponds to experiments where the degree of illumination was 7 times less.[13, 14]

Satisfying certain conditions similar to those of §2 especially (11), but in which K_3 is substituted by $K_3 n_3$, the scheme (1) can be solved approximately, putting $dn_1/dt = dn_2/dt = 0$, whence

$$K_1 n_1 = \frac{n_0 + K_3 n_3^2}{\Delta_1/A_2}; \quad K_2 n_2 = \frac{K_1 n_1}{A_2},$$

$$\frac{dn_3}{dt} = \frac{n_0}{\Delta_1} - K_4 n_3 + \frac{\Delta}{\Delta_1} K_3 n_3^2 = a - b n_3 + c n_3^2. \tag{9}$$

In the case of a nonstationary solution, i.e., when $\rho = 4ac/b^2 > 1$

$$n_2 = 2a/[\sqrt{q}\cot(\sqrt{q}/2)t + b] \quad \text{where} \quad q = 4ac - b^2 > 0 \tag{10}$$

and the reaction rate

$$K_1 n_1 \sim K_3 n_3^2.$$

According to expression (10) the reaction proceeds at first more slowly with a prolonged induction period and afterwards much more rapidly than would follow from the $e^{\phi t}$ law characteristic of a chain reaction with linear branching.

The oxidation of hydrocarbons in the cold-flame region bears a similar kinetic character, which has led Professor Neumann (of our Institute) and co-workers[15] to suppose that here also we have to deal with a quadratic branching of chains and has led him to give this hypothesis a chemical interpretation. He was also able to show that the addition of small amounts of peroxides brings down the temperature at which the cold flame appears, the effect being the more pronounced, the greater the amount of peroxide added. This would be in accord with the theory of mutual action, since the peroxides are playing the rôle of the active intermediate product.

[12] F. I. Dubovitzky, Acta Phisicochim. U.S.S.R. **2**, 761 (1935).

[13] It is no easy matter to image a scheme for the reaction H_2+O_2 which would account for quadratic branching. One of the possible solutions is:

1. $H+O_2=OH+O$; 2. $O+H_2=OH+H$;
1′. $H+O_2+M=HO_2+M$; 2′. $O+O_2+M=O_3+M$
or $O+H_2+M=H_2O+M$; 1″. H+wall; 2″. O=wall;
3. $OH+OH=HO_2+H$; 3′. $OH+H_2=H_2O+H$;
4. $OH+O_2+H_2=H_2O+HO_2$.

The difficulty is that the reaction rate for (3′) must be assumed of the same order as for (3), if not of a still lower order. The HO_2 molecules can perish on the walls. At high pressures (above the upper limit) the reaction $HO_2+H_2O=H_2O_2+OH$ can become noticeable; the latter scheme together with (4) might explain the chain of slow hydrogen oxidation at high pressures. As has been shown by N. Chirkov (reference 14).

[14] N. Chirkov, Acta Phisicochim. U.S.S.R. **6**, 915 (1937). This reaction proceeds at a rate proportional to (H_2O), so that, in the absence of water, it will be very slow. It is strange that the other workers who tried to find a mechanism for the slow oxidation of hydrogen have overlooked this circumstance.

[15] M. B. Neumann and co-workers, Acta Phisicochim. U.S.S.R. **4**, 575 (1936); **6**, 279 (1937); **9**, 861 (1938); 9, 827 (1938).

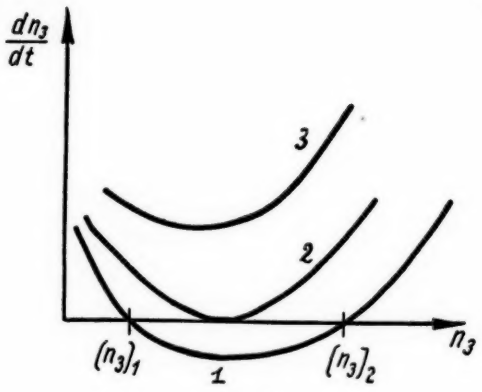


FIG. 16.

A direct proof in favor of the theory of mutual action has been obtained by Voronkov, Popilsky and myself in the oxidation of carbon disulphide.

Let us examine Eq. (9) and the physical meaning of the second root of $(n_3)_2$ in expression (5). The variation of dn_3/dt with n_3 for increasing ρ can be illustrated by curves similar to those in Fig. 16. Curve I corresponds to $\rho<1$ or $b^2>4ac$, curve 2 to $\rho=1$ or $b^2=4ac$, curve 3 to $\rho>1$ or $b^2<4ac$. Stationary solutions are obtained only for $\rho<1$. The points of intersection yield the two roots: $(n_3)_1$ and $(n_3)_2=b/c$. The first of these roots is stable, the second being unstable. Indeed, if an instantaneous concentration n_3 be produced just slightly less than $(n_3)_2$, the concentration will continue to decrease automatically until it falls to $(n_3)_1$. A concentration slightly above $(n_3)_2$ will automatically grow to infinity, so that a nonstationary state will be obtained, though b^2 is still greater than $4ac$. The physical meaning is that inflammation will set in if the experiment is conducted far from the temperature of self-inflammation, when $b^2>4ac$ and $\rho<1$, when the stationary concentration is established and the reaction rate becomes practically zero, and if the instantaneous concentration n_3 of the intermediate product is brought artificially to a value equal or greater than $(n_3)_2=b/c$.

Accordingly, a mixture of carbon disulphide and air was introduced into a long tube, one end being heated to a temperature sufficient for self-inflammation, while the remaining part of the tube was maintained at a much lower constant temperature. In the presence of mutual promoting action, the flame produced in the hot part will propagate along the cold part of the tube at the expense of the mutual action of the intermediate products which diffuse from the flame zone, attaining in the unburnt gas a concentration equal to $n_3 \geqslant (n_3)_2=b/c$. Since we used poor mixtures (0.03 percent CS_2) which, even in the case of adiabatic combustion, are able to raise the temperature by no more than some 15°, we had to deal with the influence of the possible heating of the mixture, and thus prove the isothermal nature of the propagation of the flame. It was shown that, under the above conditions, the flame travels at a constant rate, its temperature being lower by 100° than that required for the self-inflammation of the mixture in the same tube. Fig. 17 shows (1) the region of self-inflammation and (2) the region of the flame expanding in an air mixture (0.03 percent of CS_2) in a glass tube 20 mm in diameter.

Because of considerable mathematical difficulties, I did not succeed in developing an exact theory of the propagation of the flame through diffusion of the active product responsible for the quadratic branching. I therefore made use of an expression given by Frank-Kamenetzky of our Institute for the diffusional propagation of the flame when the quadratic autocatalysis is caused, not by the intermediate, but by the

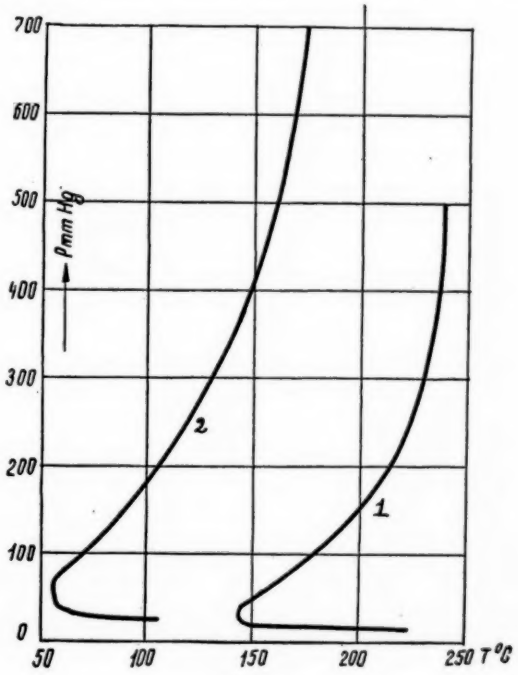


FIG. 17.

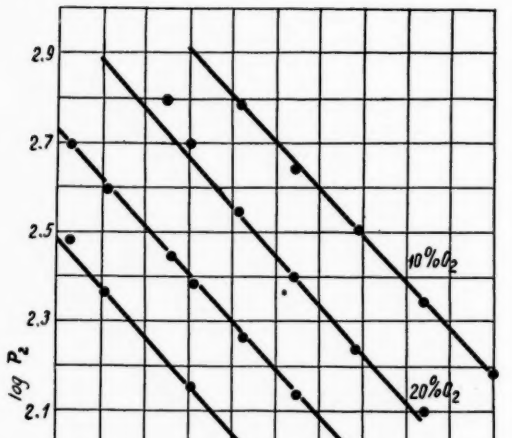


FIG. 18.

final product. It would be easy to show that this expression can be used as an approximate solution of the problem at hand. According to this expression, the rate at which the flame travels is

$$w=\left(\frac{fD}{2}\right)^{\frac{1}{2}}\left(1-2\frac{b}{f}\right), \tag{11}$$

where, as before $b=K_4$ and

$$f=c(\mathrm{CS})_0=\frac{K_3\Delta(\mathrm{CS_2})_0}{\Delta_1}.$$

$D=D_0/p$, the coefficient of the diffusion of the centers is inversely proportional to the total pressure p. $(CS_2)_0$ is the number of CS_2 molecules in the initial mixture. $\Delta=1+L-A_1A_2$ and $\Delta_1=A_1A_2-1$. Assuming that the rupture of the chain takes place only at the first link (i.e., $A_2=1$), which means that the oxygen atom begins to react as soon as $K_2+K_2'+K_2''/K_2\sim 1$ and that $L=1$, we have $\Delta=2-A_1$ and $\Delta_1=A_1-1$;

$$\frac{\Delta}{\Delta_1}=\frac{2-(K_1+K_1'+K_1'')/K_1}{(K_1+K_1'+K_1'')/K_1-1}=\frac{K_1-K_1'-K_1''}{K_1+K_1''}.$$

On the assumption that the fundamental chains are sufficiently long ($K_1\gg K_1'+K_1''$), we obtain

$$f=K_1K_3(\mathrm{CS_2})_0/(K_1'+K_2''); \tag{13}$$

considering the relation between the coefficients K and $(CS_2)_0$ and the pressure, and putting $\epsilon\ll 1$, we obtain

$$f=Ap^2/(cp^2+B), \tag{13'}$$

where A, C and B depend on the temperature, being independent of the pressure, and

$$b=K_4=gp. \tag{14}$$

The limits of the flame propagation are determined from (11) and the condition $f=2b$ or, substituting (13) into (14), from the equation

$$gcp^2-Ap+Bg=0, \tag{15}$$

which determines the boundaries of the peninsula-shaped region in which the flame expands, considering that g, c A and B depend on the temperature according to a law of the type $e^{-E/RT}$. At some distance from the end-point of the peninsula, the upper and the lower limits of propagation are determined from the expressions

$$p_1=\frac{2gB}{A} \quad \text{and} \quad p_2\frac{A}{2gc} \tag{16}$$

or

$$p_1=Pe^{+E/RT} \quad \text{and} \quad p_2Qe^{-E/RT}. \tag{17}$$

The experimental data for the upper limit fit extremely well into (17), as may be seen from Fig. 18 where the averaged experimental values are shown by circles. It will be easy to express the rate of propagation of the flame in any point inside the peninsula by the limits of propagation.

Since $D=D_0/p$, where D_0 depends on the temperature and since g depends on the temperature as $\sqrt{T}e^{-E/RT}$, we obtain

$$w=\left(\frac{fD}{2}\right)^{\frac{1}{2}}\left(1-\frac{f}{b}\right)$$

$$=K_0\frac{T}{T_0}e^{-E/RT}\frac{1-p/p_2-p_1/p}{(p_1/p+p/p_2)^{\frac{1}{2}}}. \tag{18}$$

According to experimental evidence, $E\backsimeq 0$ and b depends on the partial pressure (O_2) in a mixture of oxygen and nitrogen, $K_0=K_0'(O_2/p)$. For $T_0=410°K$, K'_{410} has been found equal to 56, whence

$$w=56\frac{(O_2)}{p}\frac{T}{410}\frac{1-p/p_2-p_1/p}{(p_1/p+p/p_2)^{\frac{1}{2}}}.$$

The above expression shows the influence of the pressure and that of the temperature on the propagation of the flame, the first in an explicit form, the other through the limits p_1 and p_2.

It must be noted that the theoretical expressions (11) and (19), similar to those for the velocity of thermal propagation of the flame, do not conform to experiment; indeed, at the limit of propagation, the velocity has a finite value, while theoretically it should be zero. In the case of the thermal theory, this discrepancy is due to the fact that no account has been taken of the heat transfer to the walls; in our case it is due to the special simplifications which had to be made when using the expression given by Frank-Kamenetzky. All the values of the limits p_1 and p_2 for (19) must therefore be found by extrapolating to zero-velocity the experimental curves showing the relationship between w and p. This operation does not present any difficulties in the case of the upper limit, the extrapolated values exceeding by some 10 percent the corresponding experimental values. In the case of the lower limit, the

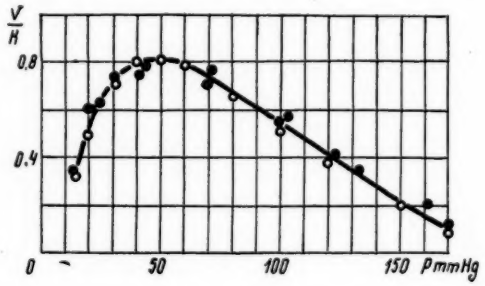


FIG. 19.

steepness of the curves renders the extrapolation doubtful, and p_1 is usually calculated from (19) from the maximum of the $w-p$ curves and the experimental value of p_2. The values of p_1 thus calculated have been found to fit quite well into (17), allowing the computation of P and E.

With the aid of the 5 constants Q, E_2, P, E_1 and K_{410} it becomes possible to calculate the

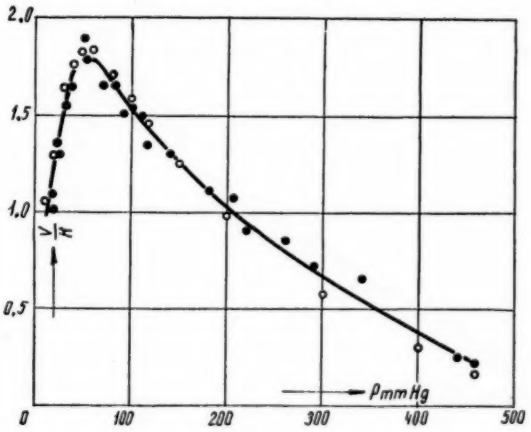


FIG. 20.

absolute values of the boundaries of the inflammation peninsula, as well as the velocities of the propagation of the flame, for any p and T inside the region of the flame expansion for mixtures with a 0.03-percent content of carbon disulphide with varying amount of oxygen and nitrogen. The two curves of Figs. 19 and 20 illustrate the good agreement between the experimental values of the velocity (marked by black circles) and those calculated (marked by white circles); one refers to a mixture of 50 percent O_2+50 percent $N_2+0.03$ percent CS_2 at $T=134°$, the other to the same mixture at $T=216°C$; the quantity v/K is plotted on the abscissae. K in the first case is 28, in the second K_1 it is 33.5.

In the case of carbon disulphide, the theory is thus seen to be supported by experimental evidence, both from a qualitative and a quantitative point of view.[16]

[16] In this brief note I must refrain from examining some extremely interesting and not yet fully explained phenomena concerning the lack of reproducibility; in some particular tubes (in no way different from others), the projecting part of the peninsula of inflammation appears as if it had been cut by a vertical line, which means that, at low temperatures, the flame does not expand. For higher temperatures, the upper and the lower limits, as well as the reaction rate, show the same numerical values as in normal tubes. Sometimes, a hitherto normal tube suddenly becomes erratic.

The Explosion of Ethyl Azide in the Presence of Diethyl Ether*

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(Received April 14, 1939)

In this paper explosion limits and induction periods for the explosion of ethyl azide in the presence of diethyl ether are reported and compared with data for pure ethyl azide. From the explosion limits certain deductions are made regarding the rate of loss of heat from the reaction flask. From the induction periods calculations of the heat of reaction are made. These give fairly consistent results over the range of temperatures, pressures, and compositions used, and are believed to offer further support to the contention that the explosion of ethyl azide is a thermal explosion. The heat of reaction found seems to be consistent with thermochemical data on related compounds. The method of calculation of the heat of reaction is applied to data of Appin, Chariton, and Todes on methyl nitrate. In this case the heat of reaction found from the explosion is inconsistent with thermochemical data, and it is concluded that the explosion of methyl nitrate cannot be a thermal explosion.

AS IS well known, when a gas which decomposes exothermally is admitted to a heated vessel an explosion will follow after a certain induction period, if the pressure is higher than a definite critical explosion pressure which depends on the temperature. An explosion occurs when the circumstances are such that the rate of production of heat by the decomposing gas is greater than the rate of removal through the walls of the vessel. Any change in conditions, such as addition of an inert gas, which affects the rate of removal of heat will therefore have an influence on the explosion. The heat capacity of the added gas, which has at most a secondary effect on the explosion limit, has a marked influence on the induction period, which is also an important characteristic of the explosion. Especially interesting results should therefore be obtained from the study of an explosion in the presence of an inert gas of large heat capacity.

The explosion of ethyl azide was investigated by Campbell and Rice[1a] and the induction period was studied by Rice, Allen and Campbell.[1b] Early in the course of these experiments it was noted that the addition of ethyl ether, a gas with a large heat capacity, caused noticeable changes in the characteristics of the explosion. These phenomena were therefore investigated in somewhat greater detail; the results will be presented in this paper.

§1. THE EXPERIMENTAL METHOD

The experiments were performed by admitting the gas mixture to be investigated into a 200-cc round Pyrex bulb held at the desired temperature in a furnace. This was done by turning a stopcock, which was held open 1 to 2 seconds, connecting the reaction bulb with a storage flask. In previous experiments the gas had to pass through about 35 cm of 6-mm (inner bore) tubing, and the stopcock was 3-mm slant bore. As we found that pressure equalization between the storage and reaction flask did not always occur in the time the stopcock could be left open, we replaced the stopcock with one with a 4-mm straight bore, and as much of the tubing as possible was replaced by 12-mm tubing. This greatly reduced the time necessary for the gas to enter the reaction chamber and establish pressure equilibrium. In other respects our apparatus and method were the same as previously described.[1,2] When an explosion occurred the induction period was measured; when no explosion occurred the rate of quiet decomposition was measured, and the critical explosion pressure was found for the mixtures used, at various temperatures.

In the case of the ethyl ether mixtures we experienced some difficulty when the pressure

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.

** Based on experimental work done in the Chemical Laboratory of Harvard University.

[1] (a) H. C. Campbell and O. K. Rice, J. Am. Chem. Soc. **57**, 1044 (1935); (b) Rice, Allen and Campbell, *ibid* **57**, 2212 (1935).

[2] A. O. Allen and O. K. Rice, J. Am. Chem. Soc. **57**, 310 (1935).

was low in deciding when an explosion had occurred. The usually audible click became so soft as to be scarcely discernible, and even the increase of pressure on explosion caused only a small jump in the manometer. This somewhat limited our range of observations.

The ethyl azide was prepared as in the earlier work. The sample was carefully prepared and coincided in its properties with the good samples of Campbell and Rice. Anhydrous diethyl ether was prepared by distillation in vacuum from the deep blue solution of pure ether and sodium benzophenone (from benzophenone and sodium-potassium alloy). The mixtures were stored in gas phase and allowed to stand at least over night to insure perfect mixing.

§2. The Explosion Limits

The data on the limiting explosion pressures for ethyl azide in the presence of ethyl ether are given in Table I. The new data on the pure azide, which were obtained as a check, are also included.

The explosion limits are shown in Fig. 1, together with the complete set of explosion limits obtained for pure ethyl azide. Actually what is plotted is not the explosion limit, P^*, itself, but instead $\log (AP^*/A_\infty T_0^3)$ is plotted against $1/T_0$, where T_0 is the absolute temperature and A/A_∞ is the ratio of the unimolecular rate constant at the pressure P^* to the limiting value of the rate constant at infinite pressure. The factor A/A_∞ allows for the effect of the falling off of the unimolecular rate with pressure. The corrections, A/A_∞, were determined from extrapolations to higher temperatures, and in a few instances to lower pressures, of Leermakers' theoretical

Table I. *Explosion limits.*

% Azide	T_0(°K)	P^*(mm)	log (A_∞/A)	log $(AP^*/A_\infty T_0^3)$
100	533.7	87.1	0.017	3.742
	547.3	24.1	.049	3.119
50.0	543.65	84.2	.013	3.707
	547.35	53.7	.017	3.499
	548.7	52.7	.017	3.488
	553.1	29.9	.025	3.222
	561.0	15.2	.046	2.889
33.4	555.0	43.3	.016	3.388
	558.9	29.7	.020	3.212
	563.0	19.2	.028	3.005
	567.55	12.5	.040	2.795

Note: P^* is partial pressure of azide.

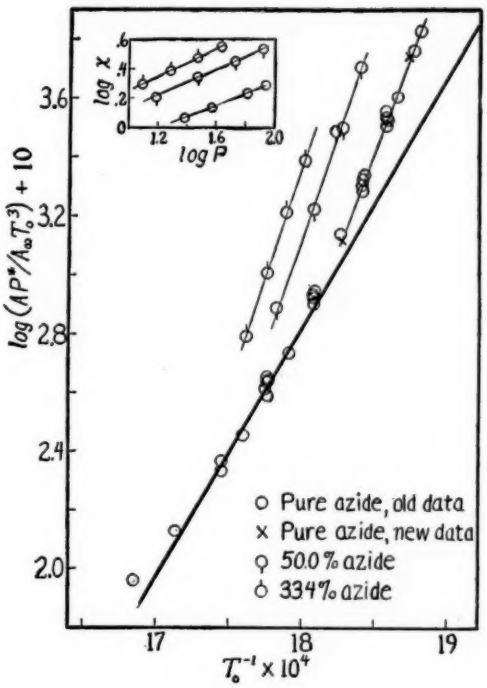


Fig. 1.

curves.[3] Since these estimates were made from the published curves they are quite rough, but, except for the two lowest points (highest temperatures) of Fig. 1, the correction is small. (The slight deviation of these points from the theoretical curve may well be due to error in this correction.) In accordance with the results on the reaction rate (see §4) it was assumed that ether had no effect on the rate of azide decomposition, except to activate azide molecules. It was assumed that ether was as effective as azide in this respect, so that A/A_∞ was calculated from the total pressure of a gas mixture.

According to Semenoff's[4] theory of thermal explosions the following relation should hold,[2] with a fair degree of approximation:

$$\log (AP^*/A_\infty T_0^3) = E/2.3RT_0 + \log x + \text{const.} \quad (1)$$

E is the energy of activation of the quiet decomposition, R is the gas constant, 2.3 is the conversion factor from natural to common logarithms, and x is the heat loss factor. The rate of loss of heat from the reaction vessel is assumed to be given by an expression of the form axT,

[3] J. A. Leermakers, J. Am. Chem. Soc. **55**, 2719 (1933).
[4] N. N. Semenoff, Zeits. f. Physik **48**, 571 (1928).

where a is the area of the wall of the vessel and T is the *difference* of temperature between the inside and the outside of the vessel, the actual temperature of the gas inside being T_0+T. According to the simple theory x is a constant, and the heavy line in Fig. 1 has the theoretical slope based on this assumption, using the previously determined value of E of 39,000 calories per mole.[1a] Actually x appears to depend upon the pressure at higher pressures. It is seen from Fig. 1 that at the higher pressures (lower temperatures) the points bend upward from the theoretical curve. In fact, the explosion limits for the ether mixtures do not show a normal dependence on temperature in any part of the available range. That this abnormal slope should continue to lower pressures in the case of the ether mixtures than in the case of the pure azide is quite to be expected, for P^* is always the partial pressure of azide, while the value of x should depend rather upon the total pressure, though it may not be independent of the nature of the added gas. It is interesting that straight lines can also be drawn through the points at higher pressures, as shown in the figure. In the case of the ether mixture, and the high pressure region of the pure azide, it may readily be shown by plotting log x, as determined from the explosion limits, against log P that $x=P^{\eta}$, where $\eta=0.39$ for pure azide, 0.45 for 50 percent azide, and 0.48 for 33.4 percent azide. (See inset, Fig. 1—the points plotted in the inset do not represent individual experiments, but are taken from the curves in Fig. 1.)

§3. The Induction Period

The induction period can be studied theoretically by considering the rate of change of temperature of the reacting gas.[1b] The rate of increase of temperature is equal to (heat produced per unit time − heat lost per unit time)/total heat capacity. The heat produced per unit time is $Qkn V$, where Q is the heat of reaction per mole, V the volume of the reaction vessel, n the number of moles of reacting gas per unit volume, and k the rate constant.

$$k=Ae^{-E/R(T+T_0)}. \tag{2}$$

We may set $n=n_0e^{-kt}$, where n_0 is the initial value of n and t is the time, provided we assume

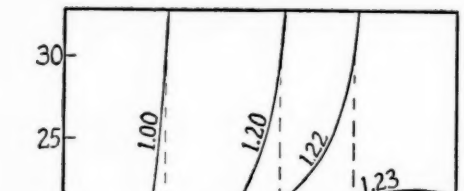


FIG. 2. The numbers on the curves give $ax/AQn_0V\times10^{17}$, hence are inversely proportional to the pressure.

as an approximation that k is constant during the induction period, an assumption which will be discussed later. The rate of loss of heat is, as we have seen, equal to axT, and the total heat capacity (assumed constant during the induction period) is n_0VC_M, where C_M is the heat capacity per mole of ethyl azide. (If there are r moles of inert gas present per mole of azide $C_M=C_A+rC_G$, where C_A is the molal heat capacity of azide and C_G that of the gas.) The relation for the rate of increase of temperature may, then, be written

$$dT/dt=A(Q/C_M)e^{-E/R(T+T_0)}e^{-kt} - (ax/n_0VC_M)T. \tag{3}$$

The qualitative character of the curves obtained by plotting T against t, starting at $t=0$ with $T=0$, can be readily understood from inspection of Eq. (3). The second term on the right-hand side of Eq. (3) starts off at zero and increases at first more rapidly, later less rapidly than the first term. Assuming the other parameters fixed, it is seen that if n_0 is sufficiently small the second term will become equal to the first, T will reach a maximum, and a quiet decomposition will occur. On the other hand, if n_0 is large, the second term will fail to become equal to the first and T will increase indefinitely. This is illustrated by Fig. 2, based on numerical integrations for

parameters corresponding approximately to possible actual conditions in the case of ethyl azide. The induction period of the explosive runs is obviously not definitely defined by Fig. 2, but for practical purposes the times indicated by the broken lines will give a sufficiently good approximation.

Since the publication of the article by Rice, Allen, and Campbell work by Todes and Appin, Chariton, and Todes[5] has appeared in which they handle the problem without making the assumption that k is constant. This leads to a pair of coupled differential equations, which can be integrated numerically. The labor involved in the numerical integration of Eq. (3) is, however, already very great, and it seems impractical to attempt to carry out this work with a sufficient range of the parameters involved to cover a wide variation of experimental conditions. An approximation method developed by Rice, Allen and Campbell may, however, be readily extended to cover all experimental conditions likely to be met with in practice, and the results can be thrown into a form in which they can be easily applied to any thermal explosion. The accuracy is probably as good as that of the usual experimental data. We shall, therefore, continue to apply this method, and present a brief résumé at this point.

In examining Fig. 2 we see that the explosive curves have an inflection point, which occurs at a value of T which is very near to $T^*=RT_0^2/E$, which is the critical increase of temperature according to the simple Semenoff theory of thermal explosions. If the value of k is to be assumed constant it is best set equal to k^*, its value at the temperature T_0+T^*, because the gas in the flask remains near this temperature longer than any other. Inspection of Fig. 2 will show that a good approximation to the induction period will be obtained by setting it equal to that time, t_c, at which T becomes equal to $2T^*$. Further, since the term e^{-kt} is in a sense a correction term, it has not been treated as a variable, but has been replaced by a sort of average value, $e^{-k^*t_c/2}$. Finally, a minor approximation has been introduced by setting $(1+T/T_0)^{-1}=1-T/T_0$, since T is small compared to T_0 over the range zero to $2T^*$. This makes possible a simplification of the first exponential factor in Eq. (3). With the approximations indicated above the solution of Eq. (3) may be written as follows:

$$t_c=(C_M/AQ)(RT_0^2/E)e^{(E/RT_0)-1}I, \qquad (4)$$

where I is a function of two important parameters, f and θ, which are defined as follows.

$$f=P^*/P, \qquad (5)$$

where P^* is the critical explosion pressure resulting from the simple Semenoff theory which neglects the factor e^{-kt} altogether. P^* is given by Eq. (1) (the constant, of course, is known in terms of the various parameters involved). P is the pressure of the given experiment, assumed greater than P^*. The parameter, θ, is given by

$$\theta=(k^*/2)(C_M/QA)(RT_0^2/E)e^{E/RT_0-1}. \qquad (6)$$

I is determined by the equation

$$I=e^{\theta I}\int_0^2 (e^{y-1}-fye^{\theta I})^{-1}dy. \qquad (7)$$

The factor $k^*/2$ in Eq. (6) comes directly from the approximation $e^{-k^*t_c/2}$ which replaces e^{-kt}. If an approximation involving a different factor than $k^*/2$ were used, θ would be proportionately changed. The only way in which the approximation enters is through the effect of θ on I. Since I does not depend strongly on θ, it thus appears that the approximation is probably sufficiently good.

If θ is zero, the premises of the theory coincide with those of the simple Semenoff theory, which neglects the reaction which takes place during the induction period. For this particular case we write I as I_0. I_0 is a function of f alone,

$$\int_0^2 (e^{y-1}-fy)^{-1}dy,$$

and can be readily obtained by numerical integration. An approximate method of obtaining I from I_0 was given by Rice, Allen and Campbell.[1] This method is based upon the fact that the integral of Eq. (7) is simply I_0 with the argument $fe^{\theta I}$. It is, as a matter of fact possible to get I exactly. Essentially the method consists in preassigning I and θ. Then it is possible to

[5] O. M. Todes, Acta Physicochim. U. R. S. S. **5**, 785 (1936). A. Appin, J. Chariton and O. M. Todes, *ibid* **5**, 655 (1936).

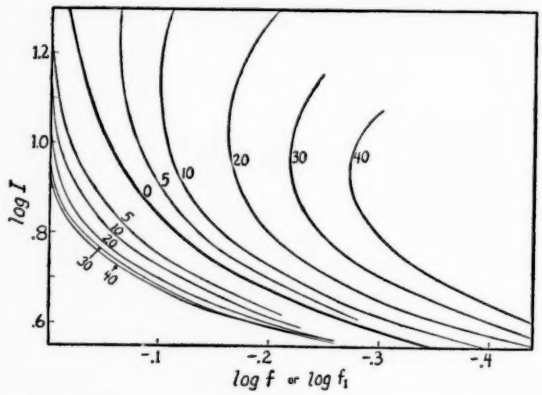


FIG. 3. The numbers on the curves give $\theta \times 10^3$. Abscissas for the curves above $\theta=0$ are $\log f$; for the curves below $\theta=0$ they are $\log f_1$. When $\theta=0$, $f=f_1$.

calculate the integral, that is, $I_0(fe^{\theta I})$ from Eq. (7). But, since I_0 is a known function of its argument, $fe^{\theta I}$ and hence f can be found. Thus, for a fixed value of θ, f can be determined as a function of I, and this functional relationship can then be reversed. The results are shown in Fig. 3, where $\log I$ is plotted as a function of $\log f$ for various values of θ (upper curves). The fact that there is a minimum for $-\log f$ means that there is a pressure below which there is no solution of Eq. (4), hence no t_c. This simply means that the explosion limit, which must be this lowest value of the pressure, does not in general coincide with the explosion limit calculated from the simple Semenoff theory. If we would get $\log I$ as a function of $\log f_1$ where

$$f_1 = P_1^*/P \tag{8}$$

and where P_1^* is the corrected (corresponding to the observed) value of the explosion limit, we must move the curves shown in Fig. 3 to the left until the minimum pressure is at the axis, as shown by the set of curves below the heavy curve. Only the lower part of each curve is retained; the upper part represents an extraneous solution which has no physical meaning.

In the preceding discussion it has been assumed that the gas starts at $t=0$ at the temperature, T_0, of the furnace (i.e., $T=0$). Of course, this is not true, and something must be added to the induction period to allow for the time it requires for the gas to be heated to the furnace temperature. If the gas starts at a temperature T_0-T', this may be accomplished, as shown by Rice, Allen, and Campbell by replacing I in Eq. (4) by $I+I'$, where

$$I' = \int_{-T'/T^*}^{0} (e^{y-1} - fy)^{-1} dy, \tag{9}$$

where $T^* = RT_0^2/E$, as before. This is based on the assumption that the factor e^{-kt} can be set equal to 1 for this pre-induction period, which is surely reasonable. Of course we are actually interested in I' as a function of f_1 rather than of f, but since the relation between f_1 and f is known the conversion is easily made.

The greatest difficulty is in deciding the value to use for T', for the gas enters the chamber rapidly through a fairly narrow tube, and so receives some preheating. Fortunately, as shown by Rice, Allen, and Campbell, I' is not extremely sensitive to T' if T'/T^* is not too small. Since T^* is about 15° this ratio should be fairly large. In our earlier work we took $T'/T^*=5$. Here, since larger tubing was used to convey the gas to the reaction chamber, we have taken $T'/T^*=10$. I' is then readily obtained by numerical integration, or, if f is sufficiently small, by expansion of the integrand as a series and term by term integration.

In the actual application of the results we have proceeded in a slightly different manner from that used previously. Substituting $I+I'$ for I in Eq. (4) we see from Eq. (6) that Eq. (4) may be thrown into the form

$$k^* t_c/2 = (I+I')\theta. \tag{10}$$

From Fig. 3, which gives I as a function of f_1 and θ, and since I' is a known function of f_1, the quantity $(I+I')\theta$ can be determined as a function of f_1 and θ. The calculated values of $I+I'$ (with $I+I'$ separate and in that order) and of $(I+I')\theta$ are given in Table II. The values of $I+I'$ are given chiefly to indicate the relative importance of I and I'; also so that I may be used separately if desired. The values of $(I+I')\theta$, which are accurate to about 1 percent, may be used directly in the comparison of any thermal explosion with the theory, provided that T'/T^* may be taken as approximately equal to 10. As t_c is determined experimentally and k^* is known[6] for any T_0 an

[6] We use $E=39{,}000$ cal. per mole and $\log A_\infty = 13.945$. This conforms with our previous work.[1a] The $\log A_\infty/A$ is obtained from Leermaker's curves,[3] as explained above. k^*, being the reaction rate at temperature T_0+T^*, where T^* is small compared to T_0, is calculated from the approximate but very nearly correct equation $k^* = Ae^{1-(E/RT_0)}$.

experimental value of $(I+I')\theta$ is obtained from Eq. (10). Since f_1 is also known for any experiment, θ can be readily determined by interpolation in Table II, which is best done graphically using curves for $(I+I')\theta$ as a function of θ with various values of f_1. Use of Eq. (6), simplified with the aid of the equation in reference 6 to give

$$\theta=(C_M/2Q)(RT_0^2/E), \qquad (11)$$

then makes it possible to obtain an experimental value of (C_M/Q). If C_M can be estimated, as is usually possible, Q can be evaluated, and its constancy from experiment to experiment may be taken as a test of the theory. Before considering the application of these equations to the actual experimental data for ethyl azide, it will be interesting to consider the qualitative behavior of t_c under various conditions. In the first place the right-hand side of Eq. (10) depends only on f_1 and θ. Now f_1 measures how far the gas pressure is from the explosion limit, while θ depends essentially only on the properties of the gas mixture studied, for the effect of temperature, according to Eq. (11), is quite small for the available range. If f_1 be fixed in advance, t_c should, for any definite mixture be inversely proportional to k^*, which is to say t_c should decrease exponentially with temperature. Secondly, it is seen from Table II that for a given θ the value of $(I+I')\theta$ decreases slightly as f_1 decreases. Hence, for fixed temperature, t_c should decrease slightly as the pressure is made to exceed the explosion limit. Finally $(I+I')\theta$ is roughly proportional to θ while θ is itself proportional to C_M. C_M, however, will increase with addition of inert gas, hence addition of such gas should increase the induction period at given T_0 and f_1.

It can be seen from inspection of the experimental data, which is presented in Table III, that all these qualitative effects are observed experimentally. In Table III the experimental values are used, in the manner indicated above, for the calculation of Q. In this calculation C_M is obtained from the value of the molal specific heat of ethyl azide of 25.3 calories per mole per degree calculated by Rice, Allen, and Campbell,[1b] together with a specific heat of 40.5 calories per mole per degree for ethyl ether.[7] Over the temperature range used variation in the specific heats may be neglected.

In making our calculations we have used both the observed value of f_1 and a value of f_1 which has been corrected for the apparent variation of the heat loss factor x with pressure, as noted at the end of §2. Instead of comparing the pressure, P, of a given experiment with the observed ex-

[7] See Landolt-Börnstein, *Tabellen*.

TABLE II.

$-\log f_1$	$\theta=0.002$	$\theta=0.005$	$\theta=0.010$	$\theta=0.020$	$\theta=0.030$	$\theta=0.040$
			Values of $I+I'$			
0.01	14.13+4.07	11.30+4.30	9.55+4.60	8.13+5.15	7.33+5.72	7.16+6.31
.02	11.48+4.13	9.66+4.38	8.37+4.70	7.18+5.25	6.73+5.85	6.61+6.44
.04	9.02+4.30	7.93+4.53	7.01+4.88	6.28+5.45	6.03+6.06	5.86+6.70
.06		6.90+4.70	6.25+5.03	5.75+5.64	5.52+6.30	5.37+6.92
.08		6.14+4.88	5.73+5.23	5.33+5.85	5.14+6.52	5.02+7.19
.10		5.65+5.04	5.36+5.41	5.01+6.07	4.81+6.77	4.73+7.46
.15			4.63+5.95	4.41+6.68	4.27+7.40	4.24+8.20
.20			4.13+6.54	3.98+7.30	3.94+8.15	3.94+9.00
.25			3.81+7.19	3.72+8.00	3.67+8.95	3.72+9.89
			Values of $(I+I')\theta\times10$.			
.01	0.364	0.780	1.415	2.656	3.92	5.39
.02	0.312	0.702	1.307	2.486	3.77	5.22
.04	0.266	0.623	1.189	2.346	3.62	5.02
.06		0.580	1.128	2.278	3.54	4.91
.08		0.551	1.096	2.236	3.50	4.89
.10		0.535	1.077	2.216	3.47	4.87
.15			1.058	2.218	3.50	4.98
.20			1.067	2.256	3.62	5.18
.25			1.100	2.344	3.79	5.45

plosion limit, P_1^*, it should be compared with the explosion limit which would result if the heat factor, instead of having the value x^* which it actually has at the pressure P_1^*, had a constant value x equal to the value at pressure P. Thus the "corrected" value of P_1^* is $P_1^* x/x^*$ and the corrected value of f_1 is accordingly $f_1 x/x^*$. Since, from §2, we know how x varies with the pressure, the correction is readily made. It does not produce any very significant change, as will be seen from Table III.

The values of Q show considerable fluctuation, but this is not surprising considering the shortness of the induction period. It would be easy to make an error of 0.1 sec. in starting the stopwatch at the beginning of an experiment, while an error of 0.2 sec. in stopping it at the time of the explosion would not seem unlikely. Another ± 0.2 sec. due to variations in the time for entry of the gas to the reaction chamber, differences in the amount of turbulence, etc., would surely not be unexpected. A variation of ± 0.5 sec. in the induction period would account for practically all the deviations from the grand average observed in Table III.

Though the time for entry of the gas is undoubtedly a source of error, we do not believe it can greatly affect our average result. This is based upon the fact that experiments in which the induction period is particularly small do not show any definite trend away from the average, and upon the reasonable agreement of the present

TABLE III. *Data and calculations on induction period.*

% AZIDE	T_0(°K)	P (MM)	t_c (SEC.)	LOG (A_∞/A)	$-$LOG f_1	Q/C_M, UNCORR.	$-$LOG $(f_1 x/x^*)$	Q/C_M, CORR.	Q, CORR. KCAL.	Q, CORR., AV.
100	533.7	89.2	4.6	0.017	0.010	2190	0.006	2410	61	
	533.7	93.3	3.8	.017	.030	2190	.018	2410	61	
	533.6	100.5	3.2	.016	.058	2190	.035	2580	65	
	547.25	25.7	2.4	.047	.026	1520	.016	1690	43	52
	547.4	26.7	2.0	.046	.048	1620	.029	1820	46	
	547.7	26.6	1.8	.046	.061	1700	.037	1910	48	
	548.0	27.1	1.8	.045	.082	1590	.050	1740	44	
	548.2	33.0	1.4	.038	.176	1860	.107	1910	48	
50.0	547.25	58.3	3.8	.016	.031	838	.017	907	60	
	547.25	63.5	3.4	.015	.068	829	.037	917	60	
	553.3	30.0	2.8	.025	.010	916	.005	985	65	
	553.2	33.1	2.4	.024	.049	875	.027	960	63	64
	553.2	39.4	2.1	.021	.124	905	.068	950	63	
	553.4	41.7	2.0	.021	.158	926	.087	950	63	
	553.05	46.0	1.9	.019	.185	997	.101	1011	67	
	560.8	19.2	1.3	.038	.092	976	.050	1055	70	
33.4	554.8	46.3	4.5	.015	.020	445	.010	477	51	
	555.0	48.1	4.3	.015	.046	425	.024	453	48	
	555.0	50.0	4.0	.015	.063	445	.033	475	50	
	555.0	51.2	3.4	.015	.073	515	.038	552	59	
	554.5	59.9	3.8	.014	.116	468	.061	483	51	51
	559.1	31.9	3.1	.020	.041	470	.021	502	53	
	563.0	20.3	2.9	.027	.024	429	.013	455	48	
	563.2	21.8	2.9	.026	.065	390	.034	410	44	
	563.1	28.8	2.2	.022	.181	492	.095	495	53	
								Grand average		55

SUPPLEMENT TO TABLE III. *Data on runs so close to explosion limit that no calculations were made. Some of these were used in determination of the explosion limit.*

100% AZIDE			50.0% AZIDE			33.4% AZIDE		
T_0	P	t_c	T_0	P	t_c	T_0	P	t_c
533.7	87.3	4.4	543.6	86.2	6.2	555.0	43.6	5.1
547.4	25.0	2.0	547.35	54.3	4.4	555.0	43.7	5.3
547.3	25.1	2.5	548.9	54.4	4.0	558.9	30.2	3.5
547.35	25.3	2.7	553.05	30.5	2.8	563.0	19.5	3.4
			561.1	16.0	1.4	567.6	12.9	2.6
			561.2	16.0	1.8			

Note: P is partial pressure of azide.

results with the rougher earlier ones[1b] for pure azide. These earlier values of Q are in general smaller, which corresponds to a larger induction period; this could be due to the inclusion in the induction period of a longer time for entry of the gas into the reaction chamber through the narrower tubing used in the earlier experiments but the discrepancy is sufficiently small to lead us to believe that no great error due to this cause remains in the experiments reported here.

The results of Table III show no significant trends, except for the fact that Q is consistently high for the 50 percent azide. This seems a little strange. It is not altogether impossible that Q should vary from mixture to mixture, for the decomposition of ethyl azide results in a complex set of products; it is likely that the products of the primary act of decomposition react with more ethyl azide, though without starting any long chain. These secondary reactions may very well be different in the presence of excess ether, which may also react with the products of the primary decomposition, so that a different value of Q would result. It is not anticipated, however, that the value of Q would reach a maximum with increasing percentage of ether and then drop off again, as is apparently observed experimentally.

§4. The Rate of the Quiet Decomposition

As noted in §1, when no explosion occurred the rate of the quiet decomposition was measured. These rates were corrected for the heating of the gas, as was done by Allen and Rice and Campbell and Rice. In so doing, however, the corrected value of P_1^*, i.e., $P_1^* x/x^*$, (approximated by $P_1^*(P/P_1^*)^{\frac{1}{2}}$) was used, as in §3, though x was assumed to remain constant through the run. The rate constants so obtained were corrected to infinite pressure. The results for the azide decomposition in presence of ether are plotted in Fig. 4. The straight line is the line which fits the points for pure azide. The results seem to run 10 to 15 percent lower than with the pure azide, but the difficulties of making the measurements are greater, and there is the possibility that the reaction is slightly complicated by side reactions between the products of the azide decomposition and the ether. On the whole, the results justify the assumption made throughout that the ether has no affect on the rate of the azide decomposition other than to activate azide molecules. It must be remembered, however, that an error in the value of k^* produces about the same percentage error in Q.

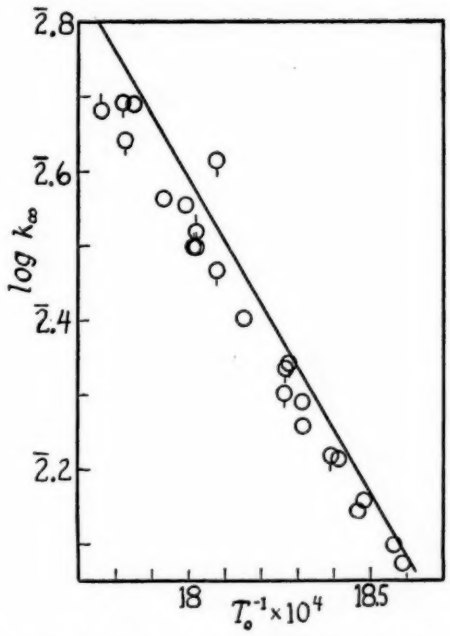


FIG. 4. The circles with a downward stroke denote 50 percent azide. Plain circles represent 50 percent azide—earlier results with less pure sample of ether (explosion data from this mixture not reported). Circles with an upward stroke denote 33.4 percent azide.

§5. Discussion

It is our belief that the data on the induction period in the presence of ethyl ether, and the check with the theory, offer one of the most convincing proofs that the explosion of ethyl azide is truly a thermal expolsion. For further confirmation it would be desirable to have independent evidence on the heat of decomposition of ethyl azide. Unfortunately no direct determination of the heat of decomposition is available, but certain thermochemical evidence does lend weight to the belief that the figure obtained from the explosion data is entirely reasonable. The reaction

$$N_3H \rightarrow \tfrac{3}{2}N_2 + \tfrac{1}{2}H_2$$

proceeds with the evolution of[7] 71 kcal., while

$$NH \rightarrow \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2$$

only gives out[8] 34. Hence it is seen that the

[8] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Co. 1936).

reaction

$$N_3H \rightarrow NH + N_2$$

is exothermic to the extent of 37 kcal. The heat of this reaction should be similar to that of

$$N_3C_2H_5 \rightarrow NC_2H_5 + N_2.$$

According to the mechanism suggested by Leermakers[3] about 80 percent of the azide decomposes through the above step, and the resulting NC_2H_5 then undergoes various reactions, which are undoubtedly exothermic, and so add to the over-all heat of reaction.[9] While it is unlikely that the mechanism is exactly that suggested by Leermakers, it seems that the net result should be about the same. It is possible that about 20 percent of the azide decomposes according to the reaction

$$N_3C_2H_5 \rightarrow C_2H_4 + N_3H,$$

which is probably endothermic (we estimate[10] 10 kcal.) but this cannot greatly affect the apparent heat of reaction, and the value obtained from the explosion data seems quite reasonable.

It is of interest to contrast this with the situation which exists in the case of methyl nitrate. In this case the quite decomposition probably proceeds according to the equation

$$CH_3ONO_2 \rightarrow \tfrac{1}{2}CH_2O + \tfrac{1}{2}CH_3OH + NO_2.$$

Because no N_2 is formed, this reaction is not nearly so exothermic as the decomposition of ethyl azide, the heat of reaction probably not exceeding 6 kcal.[5, 8] But from Appin, Chariton, and Todes' data on the induction period a heat of reaction of 70 to 80 kcal. per mole is calculated. This is far too high, and we believe that it is necessary to conclude that the explosion of methyl nitrate is not a thermal explosion after all. The discrepancy was not noticed by Appin, Chariton and Todes, because they did not make any very direct comparisons of theory and experiment. They probably failed to do this because the integrations they carried out were too complicated to be applied to a range of experimental conditions, and it is difficult to see in advance just what values of the parameters should be used.

There is another feature of the methyl nitrate explosion which does not agree with the theory of thermal explosions, nor with our experience in the case of azomethane and ethyl azide. Appin, Chariton, and Todes found, as we did, that plotting log P^*/T_0^3 against $1/T_0$ gave a straight line at high temperatures, but the slope did not coincide with that expected from the energy of activation of the thermal reaction. It is true that they made no attempt to correct for the falling off of the rate of decomposition with pressure, but this could hardly be sufficient, judging from their data on the reaction rate, to account for even a small part of the discrepancy. It has been our experience with the thermal explosions of azomethane and ethyl azide that the theoretical slope is attained at high temperatures and low pressures.

Another point of difference between the explosion of methyl nitrate and those of azomethane and ethyl azide is the effect of the surface-volume ratio of the reaction vessel. In this respect methyl nitrate is apparently much closer to the theory than are azomethane and ethyl azide.[1a, 2] However, the surface-volume ratio can have the same effect on other types of explosion, and, as there are reasons to expect variations in the heat loss "constant," x, it is not surprising that a thermal explosion should show deviations from the theory in this respect.

So, if one is prepared to grant that the explosions of azomethane and ethyl azide are thermal explosions, it would appear that these explosions have sufficiently different characteristics from that of methyl nitrate to throw doubt upon the validity of the supposition that the latter is a thermal explosion also. But the really conclusive evidence is furnished by the calculation of the heat of reaction from the induction period. We feel that it is particularly interesting that it should be possible to make a distinction of this sort from these detailed calculations, when observations of a more general type leave the matter in more or less doubt.

[9] It is, of course, the quiet decomposition which goes during the induction period and determines Q.

[10] From bond energies (tabulation of Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Co., in press)), and the difference in the heats of formation of C_2H_6 and C_2H_4.

Discussion

Guenther von Elbe, *Coal Research Laboratory, Carnegie Institute of Technology:* Any distinction between thermal and chemical chains such as described in this investigation is important, particularly in the more complicated reactions.

O. K. Rice, *University of North Carolina:* A few remarks may be made about some experimental details not reported in the paper. In certain cases there were apparently "incipient" explosions, that is, an explosion would begin, then apparently fade out, and the rest of the reaction go quietly. I have in mind two cases with 33-percent azide and 67-percent ether. One of these, at 553.1°K, partial pressure of azide 52.9 mm had an induction period of 7.5 sec., and was presumably very close to the explosion limit. The manometer showed a jump of 20 or 30 mm after which the pressure rose gradually. It is perhaps not so hard to understand a phenomenon of this type occurring very close to the explosion limit. However, in the other case I wish to report, at 556.2°K and 47.0 mm azide a similar phenomenon occurred in an experiment which was not so close to the explosion limit. I may say that these were two of a series of experiments which were not reported. They were done with a different 33-percent azide mixture, of whose composition we were slightly doubtful; the results from this mixture, however, fit in well with those reported.

In some of our early experiments we were bothered by a slight apparent decomposition of the ether, although the temperature at which ether normally decomposes is far above this. This did not occur in later experiments; we believe that it was either due to some impurity in the ether or to some substance accidentally introduced into the reaction flask which caused catalytic decomposition. It apparently did not affect the results reported.

Bernard Lewis, *U. S. Bureau of Mines:* How do you envisage the mechanism of the azide decomposition?

O. K. Rice, *University of North Carolina:* According to Leermakers, 20 percent reacts according to

$$C_2H_5N_3 \rightarrow C_2H_4 + HN_3$$

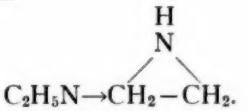
and 80 percent according to

$$C_2H_5N_3 \rightarrow C_2H_5N + N_2,$$

the latter being followed either by the reaction

$$C_2H_5N \rightarrow CH_3CH{=}NH$$

or the reaction



This cyclic compound either dimerizes to give $(C_2H_5N)_2$ or it decomposes to give $N_2+C_4H_{10}$. The reactions check with the chemical analyses which is the most important point for our purposes; the mechanisms may actually be different. There is no evidence of a chain reaction. The ethyl azide behaves in the way expected of a quasi-unimolecular reaction. Perhaps that is not sufficient evidence that it is a unimolecular reaction since there are no experiments with inert gases. However, the decomposition is at a lower temperature than azomethane, and since there is much evidence that the latter undergoes a quasi-unimolecular decomposition, it seems likely that ethyl azide follows this type of reaction also.

Guenther von Elbe, *Coal Research Laboratory, Carnegie Institute of Technology:* Is not convection a factor in the experiments?

O. K. Rice, *University of North Carolina:* Undoubtedly it plays a role in heat loss. A recent article[11] indicates that conduction is sufficient to explain the observed phenomena and that convection is unimportant, at least at low pressures. Possibly convection is important at high pressures. Our results on the heat loss constant indicate that this may be the case, but more work, both theoretical and experimental needs to be done. My impression is that thermal conduction is not enough to account for the loss of heat even at low pressures but this view may need correction.

L. S. Kassel: The amount of convection could be determined by changing the reaction vessels, using a disk-shaped vessel horizontally and vertically.

[11] Frank-Kameneckij, Comptes rendus (Doklady) Acad. Sci. U. R. S. S. **18**, 413 (1938).

Mechanisms of Complex Reactions and the Association of H and O_2*

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The kinetics of the upper explosion limit and the non-explosive thermal reaction of H_2 and O_2 uniquely demonstrates the formation of HO_2 in collisions $H+O_2+M$, its destruction on surfaces and its ability to propagate chains by gas phase reactions with H_2. Below 500° HO_2 gradually ceases to be a chain carrier in the gas phase; assuming its further reactions to be heterogeneous, involving self-neutralization and reaction with H_2, the kinetics of the mercury-photosensitized H_2-O_2 reaction are well interpreted. Bates' mechanism for this latter reaction, in which HO_2 is postulated to react in the gas phase, is shown to be inconsistent with the thermal reaction. Data on the oxygen-inhibited photosynthesis of HCl and on the H concentration in the mercury-photosensitized H_2-O_2 reaction indicate that a fraction of the associations of H and O_2 occurs in binary collisions. A quantum-mechanical treatment by Rosen shows that this process is possible. The partially binary character of the association is consistent with data on the photo-oxidation of HI. The reactions of HO_2 in a mixture of H_2, Cl_2, O_2 and HCl are discussed. Recent confirmation of the reaction $HCO+O_2=HO_2+CO$ greatly strengthens the proposed mechanism of the oxidation of aldehydes and hydrocarbons. The rate coefficient of the reaction $H+O_2+H_2=HO_2+H_2$ is found to be 0.81×10^{13} cm^6 mole^{-2} sec.$^{-1}$ at room temperature. With O_2 as a third body the rate coefficient is about $\frac{1}{3}$, and with N_2 about $\frac{1}{2}$ of this value. The rate coefficient of the reaction $H+O_2=HO_2$ is found to be 0.74×10^{8} cm^3 mole^{-1} sec.$^{-1}$ at room temperature. Comparison of the above value of the rate coefficient of $H+O_2+H_2$ with that estimated from data on the upper explosion limit shows that this reaction probably has no positive temperature coefficient, while a negative temperature coefficient is not ruled out.

THE association of H and O_2 occurs in a number of complex reactions which have been extensively investigated experimentally. However, the available material has not yet been coordinated as a whole.

1. The Evidence for the Formation of HO_2 at the Upper Explosion Limit of H_2 and O_2

Measurements of the upper explosion limit of H_2 and O_2 have shown that at constant temperature the explosion condition is accurately expressed by the equation

$$k_{H_2}(H_2)+k_{O_2}(O_2)+k_X(X)=1, \qquad (1)$$

where X denotes an inert gas, like nitrogen, and the constants k_{H_2}, etc., are independent of vessel factors.[1] Since the phenomenon of the upper explosion limit is uniquely interpreted by the isothermal branched-chain theory, the kinetic explosion condition is $\beta/\alpha=1$, where α and β are the coefficients of the net rates of chain-branching and -breaking, respectively. A relation of this form demands that all elementary reactions participating in the chain-branching and -breaking processes be of the same order with respect to the chain carriers. In the present case this can only be the first order, since no second-order branching reaction can be imagined, and higher orders are extremely improbable. If now a catalog of all imaginable first-order reactions of H, O, OH and HO_2 is written, it is possible to find eleven formal reaction schemes that lead to an explosion condition of the form of Eq. (1). However, the success of nine of these schemes rests on the assumptions that the reaction $OH+H_2+O_2=H_2O+OH+O$ or H_2O+HO_2 be much faster than $OH+H_2=H_2O+H$, and that $O+H_2+O_2=OH+HO_2$ be much faster than $O+H_2=OH+H$. These assumptions are improbable, particularly in view of the concentration conditions at the upper limit and the fact that OH and O disrupt the hydrogen molecule even at room temperature.[2,3] These nine schemes may, there-

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[1] A. A. Frost and H. N. Alyea, J. Am. Chem. Soc. **55**, 3227 (1933); G. H. Grant and C. N. Hinshelwood, Proc. Roy. Soc. **A141**, 29 (1933).

[2] G. von Elbe, J. Am. Chem. Soc. **55**, 62 (1933).

[3] H. A. Smith and G. B. Kistiakowsky, J. Am. Chem. Soc. **57**, 835 (1935).

fore, be ruled out. A tenth scheme demands the impossible assumption that $O+H_2+H_2=H_2O+2H$ be much faster than both $O+H_2+M=H_2O+M$ and $O+H_2=OH+H$. This eliminates all but the scheme:

1. $OH+H_2=H_2O+H$,
2. $H+O_2=OH+O$,
3. $O+H_2=OH+H$,
4a. $H+O_2+H_2=HO_2+H_2$,
4b. $H+O_2+O_2=HO_2+O_2$,
4c. $H+O_2+X=HO_2+X$,
5. $HO_2\rightarrow$destruction.

The explosion condition becomes

$$k_{4a}(H_2)+k_{4b}(O_2)+k_{4c}(X)=k_2, \qquad (2)$$

whence $k_{4a}/k_2=k_{H_2}$, etc. Experimentally it is found that $k_{O_2}\backsimeq\frac{1}{3}k_{H_2}$, and if the inert gas is nitrogen, $k_{N_2}\backsimeq\frac{1}{2}k_{H_2}$.

That the reactions 4, followed by 5, are the true chain-breaking reactions is shown further by the fact that there is only one alternative, namely, $O+H_2+M=H_2O+M$; this reaction, however, does not permit a solution of the problem unless it is assumed to be much faster than other reactions between O and H_2 in which the hydrogen molecule is disrupted; this is not the case even at room temperature[3] and will, therefore, certainly not be true in the much higher temperature range of the upper explosion limit (*ca.* 450–580°). HO_2 is thus formed in ternary association reactions.

Further support for the scheme comes from other sources. If N_2O is substituted for O_2 in the reacting mixture, reaction 2 should be replaced by $H+N_2O=OH+N_2$, and the chain should be continued by reaction 1. The chain carriers H and OH should, at sufficiently low pressures, be destroyed principally at the wall, as is known from the kinetics of the lower explosion limit of hydrogen and oxygen.[4] If chains are assumed to be initiated by the dissociation of N_2O into N_2 and O, which is followed by reaction 3, a scheme is obtained which is in complete agreement with the observations on the thermal reaction of N_2O and H_2 at low pressures.[5]

If traces of hydrogen are added to mixtures of carbon monoxide and oxygen, upper explosion limits are obtained over the same temperature range as for mixtures of hydrogen and oxygen.[6] According to Buckler and Norrish, the kinetics of these limits are completely described by adding the reactions $OH+CO=CO_2+H$ and $O+CO+M=CO_2+M$ to the above mechanism.

In analogy to reaction 4, it may be expected that the ternary reaction $OH+CO+O_2$ leads to the products CO_2+HO_2. Lewis and von Elbe[7] have shown that this reaction uniquely explains the oxygen-inhibition of the water-catalyzed $CO\text{-}O_2$ reaction.[8]

2. Reactions of HO_2 in Mixtures of H_2 and O_2

At the upper explosion limit the HO_2 radicals are mainly destroyed without generating other chain carriers, but as the hydrogen concentration is increased the chance for the reaction

6. $HO_2+H_2=H_2O_2+H$ (or H_2O+OH)

increases. Experimentally it is known that the chains in the slow reaction above the upper explosion limit are broken at the wall. If, now, reaction 5 is formulated as the destruction of HO_2 at the wall, reactions 1 to 6 form a scheme for this slow reaction that is in complete agreement with the extensive experimental facts.[4, 9, 10] This is perhaps the most severe test for the whole mechanism because of all the possible chain carriers H, O, OH, and HO_2, only HO_2 is available to carry on chains at pressures above the upper explosion limit. There is, in fact, no other chain carrier at all imaginable unless one resorts

[4] L. S. Kassel, "Symposium on Gaseous Combustion," Chem. Rev. **21**, 331 (1937).
[5] H. W. Melville, Proc. Roy. Soc. **A146**, 737 (1934).
[6] E. J. Buckler and R. G. W. Norrish, Proc. Roy. Soc. **A167**, 318 (1938).
[7] B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Cambridge University Press, 1938), pp. 74–77; cf. G. von Elbe and B. Lewis, J. Am. Chem. Soc. **59**, 2025 (1937).
[8] Hadman, Thompson and Hinshelwood, Proc. Roy. Soc **A137**, 87 (1932).
[9] G. von Elbe and B. Lewis, J. Am. Chem. Soc. **59**, 656 (1937); reference 7, pp. 37–52.
[10] This mechanism demands (reference 9) that the inhibition of the reaction in a silver vessel should be due to gas phase rather than surface reactions of Ag. This apparent difficulty of the mechanism has been removed. It is known that in this temperature range silver is very volatile in oxygen (C. F. Plattner, 1856, cf. Mellor, Inorg. Chem., Vol. 3, p. 343) and experiments with a silver spiral in an atmosphere of hydrogen and oxygen have shown the formation and re-evaporation of silver deposits on the wall of the vessel (H. R. Heiple and B. Lewis, unpublished).

to energy chains, as has been done in the past.[11] Such schemes have proved to be unsuccessful kinetically and are inherently implausible.

Below 500°C HO_2 gradually ceases to be a chain carrier in the gas phase, as shown by the disappearance of the chain reaction.[11] Taylor and Salley[12] have studied the mercury-photosensitized reaction between hydrogen and oxygen for a $2\,H_2+O_2$ mixture at 600 mm Hg in a closed circulatory system from 534° down to 230°C. Excited Hg dissociates H_2 in collisions of the second kind. It is of interest to compare their data with the following simple scheme which is suggested by the foregoing discussion:

$$\text{7 and 4.}\quad Hg+h\nu=Hg^*\xrightarrow{H_2}2H\xrightarrow{O_2+M}2HO_2,$$

$$\text{6.}\quad HO_2+H_2=H+[H_2O_2\rightarrow H_2O+\tfrac{1}{2}O_2],$$

$$\text{5.}\quad HO_2+HO_{2\ \text{adsorbed}}=O_2+[H_2O_2\rightarrow H_2O+\tfrac{1}{2}O_2].$$

In each run, an induction period of one to two minutes preceded the establishment of a steady state at which there is a constant rate of pressure decrease. This may be understood to be the time required to build up the surface concentration of HO_2. This surface concentration should be independent of the gas phase concentration at high values of the latter, i.e., high light intensities, and proportional to it at low values; in general it should be proportional to $(HO_2)^{x/(1+x)}$, where x increases from zero to infinity as the intensity of the absorbed light is decreased. The equation for the quantum yield becomes

$$\frac{d(H_2O)}{dt}\frac{1}{I_{abs}}=\frac{k_6(H_2)}{k_5^{(1+x)/(1+2x)}I_{abs}^{x/(1+2x)}}+1, \quad (3)$$

where I_{abs} is the intensity of the absorbed light. At temperatures in the neighborhood of 500° the quantum yield should increase strongly with temperature and should be independent of light intensity if the latter is high. This is found experimentally. If I_{abs} is small, so that x is comparable with one, the quantum yield should increase with decreasing light intensity. Three runs at 534° (marked[12] I_6, H_5 and D_5) show the existence of this effect. In agreement with Eq. (3), the effect disappears toward lower temperatures. However, in contradiction to Eq. (3), the quantum yield does not become entirely independent of temperature, but retains a slight positive temperature coefficient. This indicates that the reaction scheme is not quite complete. It may be suggested that HO_2 and H_2O_2 react at the surface with H_2, in analogy with the catalytic surface reaction of H_2 and O_2 in this temperature range.[11]

The latter suggestion leads to an interpretation of certain data of other investigators on the mercury-photosensitized reaction at or not much above room temperature.[13] These data have been interpreted previously by Bates[13] by means of the mechanism consisting of reaction 7 followed by 6 and

$$\text{8.}\quad HO_2+HO_2=H_2O_2+O_2.$$

With this scheme and data on the relative quenching efficiencies of O_2 and H_2 for Hg*, Bates showed that, in agreement with observations, the reaction rate, in a certain series of experiments,[13] should be proportional to the hydrogen pressure; that the quantum yield of H_2O_2 (this appears to be the sole product, H_2O being formed by secondary decomposition) should vary between 1 and about 3; and that, in contrast to Taylor and Salley's results in the lower temperature range, increasing light intensity should decrease the quantum yield and also the temperature coefficient of the quantum yield, as was found for the range of 50° to 100°. However, it can be shown that a scheme comprising reactions 7 and 5 and

$$\text{9.}\quad HO_{2\ \text{adsorbed}}+H_2=H_2O_2+\left[H_{\text{adsorbed}}\begin{matrix}\xrightarrow{O_2}HO_2\\ \xrightarrow{HO_2}H_2O_2\end{matrix}\right]$$

is equally consistent with the above observations. This scheme avoids the difficulty of introducing reaction 6 in this low temperature range. There still remains the problem of accounting for Taylor and Salley's observations that between 230° and about 500°C both the quantum yield

[11] C. N. Hinshelwood and A. T. Williamson, *The Reaction between Hydrogen and Oxygen* (Oxford, 1934).

[12] H. S. Taylor and D. J. Salley, J. Am. Chem. Soc. **55**, 96 (1933).

[13] J. R. Bates, J. Chem. Phys. **1**, 457 (1933). See this paper for earlier literature.

and its temperature coefficient are independent of the light intensity. It is conceivable that reaction 9 reverses its temperature coefficient and disappears and that a new reaction involving H_2O_2 and H_2 develops which would give the desired kinetic expression for Taylor and Salley's lower temperature experiments.

The idea expressed in the formulation of reactions 5 and 9 that toward lower temperatures reactions of radicals in H_2-O_2 mixtures are heterogeneous rather than homogeneous, receives further support from many experimental observations showing the activation of glass and silica surfaces by adsorption of atoms and radicals.[14]

Furthermore, it can be shown that Bates' mechanism is irreconcilable with the mechanism of the upper explosion limit. At this limit there exists the relation $k_5 \gg k_6(H_2)$. For a spherical reaction vessel $k_5 \leq \pi^2 D/r^2$, where D is the diffusion coefficient and r is the radius. The equality sign applies to the case of high surface chain breaking efficiency.[15] The explosion limit of a stoichiometric mixture of H_2 and O_2 at 856°K is at a pressure of 160 mm Hg. Judging from data on the reaction above the limit, $k_6(H_2)$ should not be larger than 0.1 k_5 at this point. D is calculated to be approximately 10 cm^2 $sec.^{-1}$. Choosing $r=2.5$ cm, which is smaller than the linear dimensions of Hinshelwood and co-workers' reaction vessels and which, therefore, increases the above inequality still further, one obtains $k_5=17$ $sec.^{-1}$ and $k_6 \ll 0.5$ mm^{-1} $sec.^{-1}$ at 24°C. The latter inequality will now be used to determine a lower limiting value for the stationary HO_2 concentration required by Bates' mechanism for the mercury-photosensitized reaction at 24°C. For this purpose the data of Farkas and Sachsse[16] are used. These investigators determined the stationary concentration of H atoms in the system by means of the para-orthohydrogen conversion in the absence of, and also in the presence of oxygen in small concentrations. In the oxygen-free system H is removed by

$$10.\quad H+H+H_2=2\,H_2.$$

Choosing from a set of their experiments at constant light intensity and constant hydrogen pressure (200 mm Hg) the value of $(H)=2\times10^{-3}$ mm Hg for the oxygen-free system and $(H)\leq 0$ for $(O_2)/(H_2)>0.1$, one obtains from Bates' mechanism and reaction 10

$$(HO_2)=n(k_{10}/k_6)\times 4\times 10^{-6}, \qquad (4)$$

where $n+1$ is the yield of H_2O_2 per quantum. Its value was estimated by Farkas and Sachsse to be about 4, in approximate agreement with earlier observations,[13] so that n becomes of the order of unity or larger. A rather reliable value of k_{10} is 1.1×10^{16} cm^6 $mole^{-2}$ $sec.^{-1}=32$ mm^{-2} $sec.^{-1}$ at 24°C,[17] whence $(HO_2)\gg 3\times10^{-4}$ mm Hg. Into this inequality there enters not only the above-mentioned factor of at least 10, but a far more important factor due to the energy of activation of reaction 6. If this is chosen as low as 8000 calories, which is far too low, a factor of about 10^4 results which brings the HO_2 pressure to the absurd value of >10 mm. This value would increase to the order of many atmospheres if a more correct value of the energy of activation were chosen.

3. Further Information on the Formation and Destruction of HO_2 from Other Kinetic Studies

(a) Oxygen-inhibited photosynthesis of HCl

Another complex reaction in which reaction 4 participates is the oxygen inhibition of the photosynthesis of hydrogen chloride. Measurements by Norrish and Ritchie[18] carried out at 25° over a wide range of concentrations of H_2, Cl_2, HCl and O_2 in some 70 experiments show that the quantum yield, γ, of HCl is described with considerable precision by the equation

$$\gamma=\frac{(Cl_2)}{(O_2)}\,\frac{3.77\times10^{-4}}{(H_2)+4(HCl)+140}, \qquad (5)$$

where the concentrations are expressed in mm Hg. This equation is valid for oxygen concentrations >10 mm except for high ratios of $(Cl_2)/(H_2)$. An equation of this form can be derived from the

[14] Farkas, Haber and Harteck, Zeits. f. Elektrochem. **36**, 711 (1930); B. Lewis, J. Am. Chem. Soc. **55**, 4001 (1933); cf. reference 7, p. 66.
[15] Reference 7, p. 41.
[16] L. Farkas and H. Sachsse, Zeits. f. physik. Chemie **B27**, 111 (1934).
[17] W. Steiner, Trans. Faraday Soc. **31**, 623 (1935); cf. I. Amdur, J. Am. Chem. Soc. **57**, 856 (1935).
[18] R. G. W. Norrish and M. Ritchie, Proc. Roy. Soc. **A140**, 713 (1933).

following scheme:

11. $Cl_2+h\nu=2Cl$,
12. $Cl+H_2=HCl+H$,
13. $H+Cl_2=HCl+Cl$,
4*a*. $H+O_2+H_2=$ chain breaking,
4*d*. $H+O_2+HCl=$ chain breaking,
4*e*. $H+O_2=$ chain breaking,

which leads to

$$\gamma=\frac{(Cl_2)}{(O_2)}\frac{2k_{13}/k_{4a}}{(H_2)+(k_{4d}/k_{4a})(HCl)+k_{4e}/k_{4a}}. \quad (6)$$

Experiments with high ratios of $(Cl_2)/(H_2)$ show that another term, $9(Cl_2)/(H_2)$, should be added to the denominator of Eq. (5), in substantial agreement with the earlier measurements of Thon.[19] A corresponding term in Eq. (6) is obtained if the reaction

14. $Cl+O_2(+M)=ClO_2(+M)$

is admitted to the scheme.[20] This term is ordinarily small and the measurements do not allow one to distinguish between the binary or ternary character of reaction 14.

A point of disagreement between Norrish and Ritchie[18] on the one side and Thon,[19] Bodenstein and Schenk[21] and Potts and Rollefson[22] on the other is the introduction of the reaction

$$H+HCl^{\bullet}=H_2+Cl$$

which Norrish and Ritchie consider necessary and which introduces a fifth term of the form $(HCl)/(H_2)$ in the denominator of Eq. (6). Since all authors agree that this term is in any case unimportant in the oxygen-inhibited reaction it can be dismissed here.

At small oxygen concentrations other chain-breaking reactions, such as the recombination of the Cl atoms and their destruction at the wall, come into prominence, and Eqs. (5) and (6) must be suitably modified.[18]

In the above scheme reactions 11, 12 and 13 have long been known to occur. Reaction 4*a* yields HO_2; while in reaction 4*d*, where HCl is the third body, products other than HO_2+HCl are not ruled out. This, however, is a minor question compared to the problem presented by the binary character of reaction 4*e*. This problem becomes apparent only from Norrish and Ritchie's work, since in the other investigations the pressure variations have not been carried far enough. Norrish and Ritchie's experimental quantum yields demand the retention of this reaction as written, or a series of kinetically equivalent reactions;[23] for, (1) if 4*e* is omitted, or (2) if it is written as a ternary reaction with O_2 or Cl_2 or both as third bodies (H_2 and HCl already appear as third bodies in 4*a* and 4*d*), the coefficients of the corresponding kinetic equation cannot be adapted to the experimental values of the quantum yield. The best average, as obtained by the method of least squares, leads to differences between calculated and experimental values of γ of over 50 percent in a large fraction of the experiments. Eq. (5), on the other hand, seldom leads to differences of more than a few percent, and in no case of more than 14 percent.

The hypothesis that the association of H and O_2 occurs partly in binary and partly in ternary collisions receives support from the quantum mechanical treatment of a simplified HO_2 model by Rosen.[24] He showed that if the total energy in the system HO_2 is but little more than that needed for dissociation, there exist discrete quantum states representing the distribution of the energy between the OH and OO bonds for which the average lifetime is very short (10^{-10} to 10^{-14} sec.), and others, for which the lifetime is large enough ($>10^{-8}$ sec.) to permit stabilization in subsequent collisions. In view of the difficulties of kinetic alternatives, as described in reference

[19] N. Thon, Zeits. f. physik. Chemie **124**, 332 (1926).
[20] A kinetic alternative to reaction 14 is *x*. $H+O_2+Cl_2\rightarrow X$; *y*. $X+H_2\rightarrow$chain carrier; and *z*. $X\rightarrow$destruction (unimolecular) where X is an intermediate and $k_y(H_2)\gg k_z$.
[21] M. Bodenstein and P. W. Schenk, Zeits. f. physik. Chemie **B20**, 420 (1933).
[22] J. C. Potts and G. K. Rollefson, J. Am. Chem. Soc. **57**, 1027 (1935).
[23] Such a series of reactions can be formulated on the principle that an intermediate substance X is formed, without loss or gain of chain carriers, whose steady-state concentration is substantially proportional to the product $(H)(O_2)$, and which is destroyed at a unimolecular rate (either by decomposition in the gas phase or at the wall with a surface efficiency sufficiently small so that the influence of the total pressure is negligible; cf. reference 7, p. 25). An example is the following scheme: *x*. $Cl+O_2+H_2\rightarrow X$; *y*. $X+Cl_2\rightarrow H$ or Cl; and *z*. $X\rightarrow$destruction (unimolecular) where $k_y\gg k_z$. It is difficult to identify X with a plausible compound. Variations of the above principle present even greater difficulties.
[24] N. Rosen, J. Chem. Phys. **1**, 319 (1933).

23, the above hypothesis becomes very plausible, and one may write

$$4e.\ H+O_2=HO_2.$$

Since O_2 may act as a third body, it is necessary to admit the reaction

$$4b.\ H+O_2+O_2=HO_2+O_2$$

to the scheme. The occurrence of reaction

$$4f.\ H+O_2+Cl_2=HO_2+Cl_2$$

is problematical, since the products may also consist, for example, of $HCl+Cl+O_2$, in which case the chain is not broken. An analysis of Norrish and Ritchie's data shows that both 4b and 4f may be admitted to the scheme without disturbing the agreement between the calculated and experimental quantum yields, if the values of the other coefficients are adjusted slightly. If only 4*b* is admitted, k_{4b} can be as large as *ca.* $0.2k_{4a}$ (see, however, below), while the coefficients k_{4d}/k_{4a}, k_{4e}/k_{4a}, $2k_{13}/k_{4a}$ in Eq. (6) may assume values within the ranges 4.24 to 4.67, 144 to 176 mm Hg, 3.79×10^{-4} to 4.17×10^{-4} mm Hg, respectively, at 25°C.

The further reactions of the radical HO_2 in a mixture of H_2, Cl_2, HCl and O_2 must be so postulated that they are consistent with previously discussed reactions and, (1) Eq. (6), modified to include reaction 4b, (2) the observation of Bodenstein and Schenk[21] that in mixtures not over-rich in HCl the yield of H_2O per chain is approximately equal to the fraction

$$[(H_2)+0.2(HCl)]/[(H_2)+0.2(HCl)+3(Cl_2)],$$

and (3) the observation of Krauskopf and Rollefson[25] that on simultaneously decreasing the chlorine concentration and increasing the oxygen concentration the ratio of the yields of H_2O to HCl increases roughly to the limit 1, and can be raised above 1 by large increases in the HCl concentration. These requirements are met, for example, by the following reactions:

$$15.\ HO_2+Cl_2=HCl+\left[ClO_2\xrightarrow{Cl}Cl_2+O_2\right]$$

$$16.\ HO_{2\ \text{adsorbed}}+HCl=Cl_{\text{adsorbed}}+\left[H_2O_2\xrightarrow{Cl}H_2O+ClO\right],$$

$$7.\ HO_{2\ \text{adsorbed}}+H_2=H_{\text{adsorbed}}+\left[H_2O_2\xrightarrow{Cl}H_2O+ClO\right],$$

possibly followed by

$$17.\ HO_2+Cl_{\text{adsorbed}}=HO_2Cl\xrightarrow{Cl}ClO+\left[HOCl\xrightarrow{HCl}H_2O+Cl_2\right],$$

$$5a.\ HO_2+H_{\text{adsorbed}}=H_2O_2\xrightarrow{Cl}H_2O+ClO,$$

$$18.\ ClO\rightarrow\tfrac{1}{2}Cl_2+\tfrac{1}{2}O_2.$$

The reaction $H_2O_2+Cl=H_2O+ClO$ is supported by Bodenstein and Schenk's observation that H_2O_2 is destroyed by chlorine atoms. H_2O_2 has been detected in the reacting mixture by Norrish,[26] using the sensitive titanic acid test. Assuming, therefore, that Cl is destroyed by H_2O_2, reactions 15 and 17 must also lead to the destruction of a chain carrier, as indicated, or else additional terms depending on the concentration of the reactants would be introduced in the denominator of Eq. (6) and it would be impossible to adapt the coefficients of this equation to the experimental quantum yields. The H_2O yields of Bodenstein and Schenk are correctly represented if $k_{15}\simeq 6k_7$, and $k_{16}\simeq 0.2k_7$. At very low Cl_2 and high O_2 concentrations, reactions 13 and 15 become negligible, which leads in the limit to a ratio (H_2O/HCl) formed of 1 or more. Bodenstein and Schenk have proposed a scheme of HO_2 reactions which conflicts with the latter requirement because they allow, for these conditions, the destruction of one or more HCl for every HO_2 formed.

The compound ClO_2, as prepared from chlorates, can be detected spectroscopically in extremely small concentrations, but it has not been found in the irradiated mixture of H_2, O_2 and Cl_2.[21] Bodenstein and Schenk suggest that the compound formed in reaction 14 may be an isomer. This would also apply to the ClO_2 formed in reaction 15.

Although the above scheme of HO_2 reactions is speculative, it is experimentally certain that there exists one reaction path, 15, of HO_2 in which no H_2O is formed and which, therefore,

[25] K. B. Krauskopf and G. K. Rollefson, J. Am. Chem. Soc. **56**, 327 (1934).

[26] R. G. W. Norrish, Trans. Faraday Soc. **27**, 461 (1931).

very probably involves the destruction of Cl_2 and the formation of HCl. This increases the quantum yield by two for sufficiently large ratios $(Cl_2)/(H_2)$. Adding to it the hitherto neglected destruction of $1Cl_2$ in the photodissociation, the total correction becomes three. This correction is not negligible in experiments where the chains are short, i.e., large ratios $(O_2)/(Cl_2)$, and it leads to an improved agreement between the calculated and experimental quantum yields in such experiments of Norrish and Ritchie. It also makes it possible to admit $k_{4b} \leq 0.3k_{4a}$, which is the same ratio found for these quantities at the upper explosion limit of H_2 and O_2.[1]

(b) H atom concentrations in mercury-photosensitized H_2-O_2 reaction

The occurrence of the binary reaction 4*e* is strikingly confirmed by Farkas and Sachsse's[16] measurements of hydrogen atom concentrations in the mercury-photosensitized H_2-O_2 reaction at 200 and 500 mm total pressure and constant light intensity. The reactions to be considered are 7, 10, 4*a* and 4*e*. Reaction 4*b* can be neglected since the percentage of oxygen in the mixture is very small. The kinetic equations are: (a), in the absence of oxygen, since H is destroyed only by reaction 10,

$$2I_{abs} = k_{10}(H_0)^2(H_2), \tag{7}$$

where the subscript 0 refers to the oxygen-free mixture; and (b), in the presence of oxygen

$$2I_{abs} = k_{10}(H)^2(H_2) + k_{4a}(H)(O_2)(H_2) + k_{4e}(H)(O_2), \tag{8}$$

whence

$$\frac{k_{10}}{k_{4a}} = \frac{(H)(O_2)}{(H_0)^2 - (H)^2}\left(1 + \frac{k_{4e}}{k_{4a}(H_2)}\right). \tag{9}$$

By combining two Eqs. (9) for values of H and H_0 at 200 and 500 mm total pressure, k_{10}/k_{4a} can be eliminated and

$$\frac{k_{4e}}{k_{4a}} = \frac{\dfrac{(H)_{500}}{(H)_{200}} - \dfrac{(H_0)^2_{500} - (H)^2_{500}}{(H_0)^2_{200} - (H)^2_{200}}}{\dfrac{1}{200}\dfrac{(H_0)^2_{500} - (H)^2_{500}}{(H_0)^2_{200} - (H)^2_{200}} - \dfrac{1}{500}\dfrac{(H)_{500}}{(H)_{200}}}, \tag{10}$$

where all concentrations are expressed in mm Hg at 24°.

Table I contains data read from Farkas and Sachsse's Fig. 5, and the calculated values of k_{4e}/k_{4a} and k_{10}/k_{4a}. The values of k_{4e}/k_{4a} are in excellent agreement with the values of 144–176 found above from the oxygen inhibition of the photosynthesis of HCl.

From $k_{10}/k_{4a} = 1327$ and Steiner's[17] value of $k_{10} = 1.1 \times 10^{16}$ cm^6 mole^{-2} sec.$^{-1}$ one obtains $k_{4a} = 0.83 \times 10^{13}$ cm^6 mole^{-2} sec.$^{-1}$ It is of interest to compare this value with a value of k_{4a} estimated from data at the upper explosion limit. Reaction 4*e* does not alter the form of the explosion condition at the upper explosion limit. k_2 in Eq. (2) now becomes $k_2 - k_{4e}$. It may be supposed, however, that 4*e* does not occur to any great extent at these high temperatures since the fraction of low energy collisions decreases with increasing temperature. For a stoichiometric mixture, using $k_{4b} = 0.3k_{4a}$ and neglecting k_{4e}, the explosion condition is

$$k_2 = 1.15k_{4a}(H_2). \tag{11}$$

If reaction 4 is assumed to have no energy of activation, the energy of activation of reaction 2 is obtained from the observed pressure and temperature relations of the upper limit and equals about 26,000 cal.[27] If k_2 is set equal to $f \times Z \times \exp -(26{,}000/RT)$, where f is the "steric factor" and Z the collision frequency, then at 856°K where the explosion limit is 160 mm $k_{4a} \leq f \times 7.5 \times 10^{13}$ cm^6 mole^{-2} sec.$^{-1}$. Since $f < 1$ this suggests that reaction 4 has no positive temperature coefficient, while a negative temperature coefficient is not ruled out.

(c) Photo-oxidation of HI

The photodissociation of HI in the presence of O_2 leads to H_2, I_2, and H_2O_2.[28] Since the photo-act leads to H and I,[29] the reaction scheme is uniquely given by

$$\begin{aligned} &HI + h\nu = H + I, \\ &H + HI = H_2 + I, \\ 4.\ &H + O_2(+M) = HO_2(+M), \\ &HO_2 + HI = H_2O_2 + I. \end{aligned}$$

Measurements by Cook and Bates[28] of the yields of H_2O_2 and H_2 showed that addition of

[27] G. H. Grant and C. N. Hinshelwood, reference 1.

[28] J. R. Bates and G. I. Lavin, J. Am. Chem. Soc. **55**, 81 (1933); G. A. Cook and J. R. Bates, *ibid.* **57**, 1775 (1935).

[29] B. Lewis, Nature **119**, 493 (1927); J. Phys. Chem. **23**, 270 (1928). K. F. Bonhoeffer and L. Farkas, Zeits. f. physik. Chemie **132**, 235 (1928).

TABLE I. *Calculation of k_{4e}/k_{4a} and k_{10}/k_{4a} from Farkas and Sachsse's measurements of the* H *concentration in the mercury-photosensitized* H_2-O_2 *reaction at 24°.*

$(H_2)=200$ MM $(H_0)=2\times10^{-3}$ MM (H) $\times10^{-3}$, MM	$(H_2)=500$ MM $(H_0)=1.264\times10^{-3}$ MM (H) $\times10^{3}$, MM	(O_2), MM	k_{4e}/k_{4a}, MM	k_{10}/k_{4a}
0.390	0.21	6.15	143	1069
0.635	0.36	3.75	174	1234
0.860	0.50	2.74	187	1400
0.950	0.55	2.51	172	1430
1.065	0.62	2.21	165	1500
			Average 168	1327

nitrogen increases the ratio H_2O_2/H_2, thus confirming the partly ternary character of reaction 4. A comparison of the experimental and theoretical yields of these substances (including reaction 4*e* in the above scheme) shows that N_2 is about 1.5 to 2 times more effective as a third body than O_2. This is about the same relative effectiveness of these molecules that exists at the upper explosion limit of H_2 and O_2.[30]

(d) The oxidation of formaldehyde and methane

Experiments on the photolysis and the photo-oxidation of acetaldehyde make it practically certain that this molecule is oxidized to peracid by the following chain reaction:

$$CH_3CO \xrightarrow{O_2} CH_3CO(OO) \xrightarrow{CH_3CHO} CH_3CO(OOH) + CH_3CO.$$[31]

The photo-oxidation of formaldehyde is also a chain reaction, but in contrast to the photo-oxidation of acetaldehyde, no peracid is formed. The main products are formic acid, CO and H_2O.[32] Lewis and von Elbe[33] have interpreted this difference in the products by assuming that the radical HCO, which is the analog to CH_3CO in the acetaldehyde chain, is incapable of adding O_2 to form a peracid radical, but that it reacts according to

$$19.\quad HCO+O_2=HO_2+CO,$$

followed by

$$20.\quad HO_2+HCHO=HCOOH+OH,$$
$$OH+HCHO=H_2O+HCO.$$

Reaction 19 has since been confirmed by Harteck, Groth and Faltings[34] in experiments on the mercury-sensitized reaction between H_2 and CO in the presence of traces of oxygen: While in the oxygen-free mixture the only product is formaldehyde which involves the intermediate formation of HCO by the association of H and CO in a three-body reaction,[16] a trace of O_2 (<0.1 percent) suppresses the formation of formaldehyde and yields, instead, H_2O_2. In the absence of CO, much higher percentages of O_2 are required in an H_2-O_2 mixture to yield detectable amounts of H_2O_2,[16, 34] the H atoms being destroyed mainly by recombination. In explaining these facts no alternative to reaction 19 is apparent.

At high temperatures reaction 20 leads to CO and H_2O instead of formic acid. With the mechanism of the formaldehyde oxidation thus substantiated, the mechanism of the thermal oxidation of methane[35] is likewise confirmed since monovalent radicals are present and the main products are formaldehyde, CO and H_2O. The chain reactions are

$$OH+CH_4=H_2O+CH_3,$$
$$CH_3+O_2=HCHO+OH,$$
$$OH+HCHO=H_2O+HCO,$$
$$19.\quad HCO+O_2=CO+HO_2,$$
$$20a.\quad HO_2+HCHO=CO+H_2O+OH.$$

On the basis of this mechanism and other analytical and kinetic information, the proposed chain reactions in the oxidation of higher hydrocarbons[36] are well supported.

[30] A. A. Frost and H. N. Alyea, reference 1.
[31] Reference 7, p. 84.
[32] J. E. Carruthers and R. G. W. Norrish, J. Chem. Soc. 1036 (1936).
[33] Reference 7, pp. 85–86.
[34] Harteck, Groth and Faltings, Zeits. f. Elektrochem. **44**, 621 (1938).
[35] G. von Elbe and B. Lewis, J. Am. Chem. Soc. **59**, 976 (1937); cf. reference 7, p. 89.
[36] Reference 7, Chapter 4.

Discussion

J. A. Christiansen, *Polytechnic Chemical Institute, Copenhagen:* This reaction scheme seems to be consistent with all the facts. Such correlation of all the facts has been accomplished only for a few reactions. We should perhaps study fewer reactions but investigate them more thoroughly.

What we can do is to study the kinetics of the resultant reaction over a wide range of conditions and then find out which sequence (or sequences) of component reactions would lead to the kinetics actually found by experiment.

O. K. Rice, *University of North Carolina:* When HO_2 is formed, the energy can fluctuate from one degree of freedom to another and there is always sufficient energy to cause decomposition. It would seem that the fluctuation and the concentration of that energy in one bond would take place more quickly than the quantum transition considered by Rosen. I think that the suggested life period of 10^{-8} second is entirely too long from a theoretical point of view.

Guenther von Elbe, *Coal Research Laboratory, Carnegie Institute of Technology:* Might it not still be possible that a small fraction of the collision complexes have the required lifetime? The rate of binary association is supposed to be as fast as the rate of ternary association in collisions $H+O_2+H_2$ at 168 mm of hydrogen.

Kinetics of the Oxidation of Hydrogen Sensitized by Nitrogen Dioxide*

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The effect of small amounts of nitric oxide in lowering the explosion limits of the oxidation of carbon monoxide has been studied. The investigation has been extended to the study of the oxidation of hydrogen. The influence of walls, temperature and relative concentration of materials on the reaction rate has been studied. The results are explained on the assumption that NO_3 is an important intermediate product in both the carbon monoxide and the hydrogen oxidations. The influence of adsorption by the walls is emphasized.

THE unusual effect of small amounts of nitrogen dioxide in lowering the explosion limits of mixtures of oxygen with hydrogen and with carbon monoxide has excited considerable interest since its discovery.[1] The explosion limits have been established with considerable accuracy. An explanation for the phenomenon was sought early in the branching chain theory of explosions. In connection with the origin of chains Norrish and others[2] found that the rate in the region of the explosion limits was considerably increased on illumination with light of a wave-length which from the character of the spectrum would produce nitric oxide and oxygen atoms. A thermal reaction of this nature is somewhat difficult to establish. However, it is a convenience of the explosion theory that a mechanism can be devised without requiring a description of the chain origin. On such a basis von Elbe and Lewis[3] have set up a theory for the hydrogen case.

It was shown by Crist and Roehling[4] that in the carbon monoxide system a reaction of measurable rate set in above the upper critical limit. The later investigation of Calhoun and Crist[5] established this phase of the reaction as homogeneous and the one in the explosion region as dependent on the nature of the vessel. This heterogeneous character is shown in the inset of Fig. 1. To investigate the kinetics of the homogeneous reaction the usual expedient of having one component relatively very large gave satisfactory results. It was found that with a mixture such as $CO=600$ mm, $O_2=20$ mm, $NO=10$ mm that the rate was first order with respect to oxygen. This indicated that the effect of the oxide of nitrogen was constant during each single run. These first-order oxygen constants (indicated by k') were found to vary linearly with the nitric oxide introduced. Also, carbon monoxide when decreased from 600 to 300 mm had no effect. To account for these results as well as for those reported here for hydrogen, the following reactions were assumed.

Oxidation of Carbon Monoxide

$$NO+O_2\rightarrow NO_3, \quad (1)$$

$$NO_3+CO\rightarrow NO_2+CO_2, \quad (2a)$$

$$NO_2+CO\rightarrow NO+CO_2, \quad (3a)$$

$$2NO_2\rightarrow 2NO+O_2. \quad (4)$$

Oxidation of Hydrogen

$$NO_3+H_2\rightarrow NO_2+H_2O, \quad (2b)$$

$$NO_2+H_2\rightarrow NO+H_2O, \quad (3b)$$

If we assume (2a) to be fast compared to (1) then the rate constant (k_1) of the latter can be obtained from the slope of the plot of k' against the concentration of nitric oxide. The temperature dependence of constants so obtained is shown in curve A of Fig. 2. This very small effect of temperature suggests that we may be dealing

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** Deceased. The experimental work presented in this paper was carried out by him.

[1] See B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Cambridge University Press, 1938), pp. 56 and 77 for general references.

[2] Norrish and Griffiths, Proc. Roy. Soc. **A139**, 147 (1933); Foord and Norrish, *ibid.* **A152**, 196 (1935).

[3] G. von Elbe and B. Lewis, J. Am. Chem. Soc. **59**, 2022 (1937).

[4] R. H. Crist and O. C. Roehling, J. Am. Chem. Soc. **57**, 2196 (1935).

[5] G. M. Calhoun and R. H. Crist, J. Chem. Phys. **5**, 301 (1937).

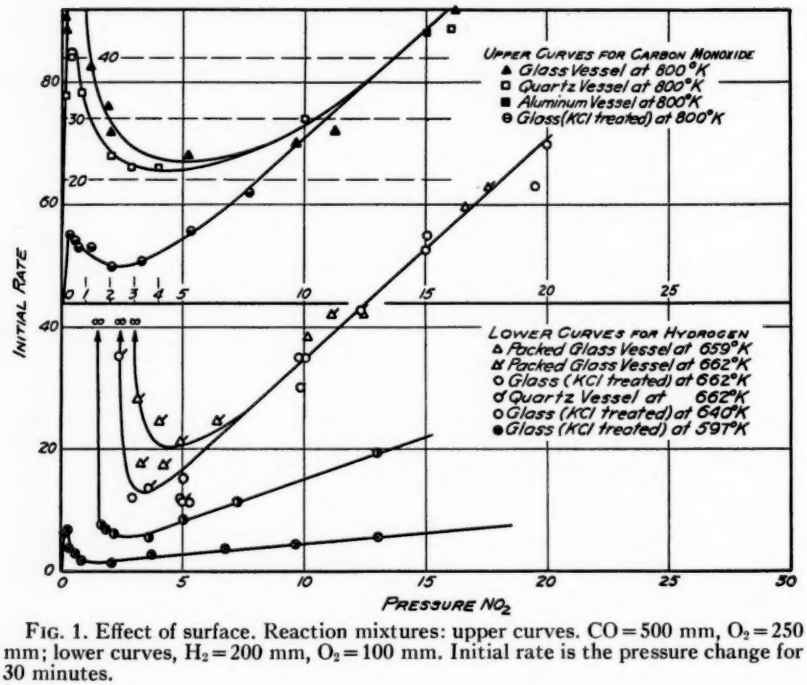
Upper Curves for Carbon Monoxide
▲ Glass Vessel at 800°K
□ Quartz Vessel at 800°K
■ Aluminum Vessel at 800°K
⊖ Glass (KCl treated) at 800°K
Lower Curves for Hydrogen
△ Packed Glass Vessel at 659°K
✕ Packed Glass Vessel at 662°K
○ Glass (KCl treated) at 662°K
✕ Quartz Vessel at 662°K
○ Glass (KCl treated) at 640°K
● Glass (KCl treated) at 597°K
Initial Rate
Pressure NO2

FIG. 1. Effect of surface. Reaction mixtures: upper curves. CO = 500 mm, O_2 = 250 mm; lower curves, H_2 = 200 mm, O_2 = 100 mm. Initial rate is the pressure change for 30 minutes.

with a reaction responsible for the low temperature dependence of the ordinary oxidation of nitric oxide. For this, reaction (2a) would be changed to

$$NO + NO_3 \rightarrow 2NO_2. \qquad (5)$$

Then if we assume (1) to be in reversible equilibrium under the conditions of the experiment the third-order constant obtained by Bodenstein would result.

The plausibility of the assumption of the oxide NO_3 is indicated by its use in explaining other kinetic results. Further it has been prepared and its properties described.[6]

Reactions in Hydrogen Mixtures

The values of k_1 were shown to be independent of carbon monoxide but it seemed advisable to confirm this by the use of another substance that could serve in the same manner. Hydrogen was selected for this purpose and the results will be given in detail. The temperature range for which satisfactory results can be obtained is determined by the relative reaction rates. For (1) to be the rate determining reaction (2b) must be fast compared to (1) and (5). A test for this will be the linear relation between k' and nitric oxide. Also, (3b) and (4) must be fast compared to (1) so that the nitric oxide present is equal to the original nitrogen dioxide. The test for this will be the constancy of k' values for single runs. These conditions were satisfied for the carbon monoxide system between 658 and 800°K and for hydrogen between 657 and 717°K.

The experiments with hydrogen were carried out in a manner similar to those for carbon monoxide. The hydrogen was prepared electrolytically and purified in the usual way. Unless otherwise noted oxygen was introduced first into the reaction vessel and was followed by nitrogen dioxide and hydrogen. The temperature was controlled by a liquid vapor thermostat.

For the purpose of this study it was essential to determine the effect of the surface. The reaction vessels used were as follows: (1) Pyrex, rinsed with a saturated solution of potassium chloride and dried, vol. = 220 cc; (2) packed Pyrex, vol. = 185 cc, surface volume ratio, $S/V = 4.8$; (3) Pyrex, vol. = 184 cc, $S/V = 2.3$;

[6] For its use in the sensitized decomposition of ozone see Schumacher and Sprenger, Zeits. f. physik. Chemie **A136**, 77 (1938); **B12**, 267 (1929). See also G. von Elbe and B. Lewis, reference 3, for its use in the oxygen hydrogen explosion mechanism, and their reference 12 for its preparation and properties.

(4) quartz, packed with quartz tubing with closed ends, vol. = 177 cc. The reaction mixture was 200 mm of hydrogen and 100 mm of oxygen and varying amounts of nitrogen dioxide. The results are shown in Fig. 1. The lower limit was difficult or impossible to determine. The upper limit is affected by the nature of the vessel though as seen in the figure this effect appears to be much less than for carbon monoxide. However, the two sets are not entirely comparable because of the total pressure and temperature differences in the two cases. It is likely that the surface effect involves nitric oxide and oxygen in which case the hydrogen in a region of comparable rates also would show the greater surface dependence. The limits at 662°K compare favorably with those determined by Hinshelwood. The results were not as reproducible as those for carbon monoxide.

The kinetics of the reaction above the upper limit were investigated by the use of mixtures of 500 mm of hydrogen, 25 mm of oxygen and 15 to 25 mm of nitrogen dioxide. The rate was strictly first order with respect to oxygen over some three-fourths of the run.* A few runs were made with 300 mm of hydrogen, other conditions remaining the same, and the constants were unaffected. The first-order constants for oxygen were then used to obtain the k_1 values given in Table I. These are shown in curve *C* of Fig. 2 as a function of temperature. The whole curve is considerably higher and shows a greater temperature dependence than that (curve *A*) for

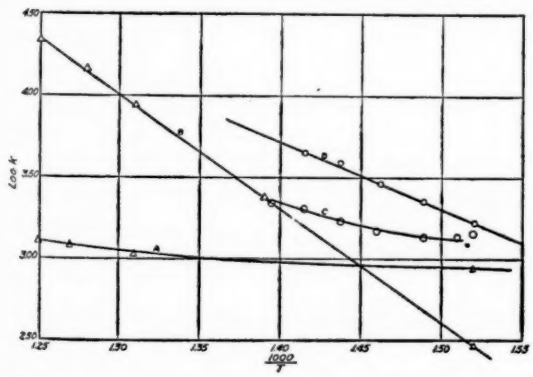

FIG. 2. Temperature dependence of the velocity constants. *A*, k_1 for CO; *B*, k_{3a} for CO; *C*, k_1 for H_2; *D*, k_{3b} for H_2.

* A small contribution to the original oxygen added came from the nitrogen dioxide. See G. M. Calhoun and R. H. Crist, reference 5.

TABLE I. *The temperature dependence of* k_1 *and* k_{3b}.

TEMP. °K	$k_1 \times 10^{-3}$	$k_{3b} \times 10^{-3}$
657	1.46	1.66
662	1.36	
670	1.35	2.24
684	1.49	2.87
696	1.73	3.86
707	2.00	4.45
717	2.18	

carbon monoxide. To make certain that the differences were not due to experimental conditions the experiments for carbon monoxide at 658°K were repeated and found to check the original work. The character of the two curves of Fig. 2 suggests that the essential process is the same but that for hydrogen there is superimposed a reaction with a higher temperature coefficient. Above 716°K the effect is sufficient to cause marked deviations in the k_1's. Also, a more careful study at 662°K showed an appreciable surface reaction. The results are given in Table II. There is an increase of eight percent in the constant as a result of the change of surface. Also, there seems to be a definite trend in the case of the packed Pyrex vessel. This effect may well increase rapidly with temperature and account for the higher temperature coefficient observed as well as for the inability to obtain good k_1 values at temperatures much above 716°K.

We now turn to the results obtained under conditions where the oxides of nitrogen are maintained in their equilibrium concentrations, namely, with mixtures of 500 mm of oxygen, 10 to 25 mm of total nitrogen oxides and 25 to 30 mm of hydrogen. The rates are first order with

TABLE II. *Surface reaction at 662°K,* $H_2 = 500$ *mm,* $O_2 = 30$ *mm,* NO *as indicated.*

CELL TREATED WITH KCl		PACKED PYREX CELL, $S/V = 4.8/1$	
PRESS. NO (MM)	$k_1 \times 10^{-3}$	PRESS. NO (MM)	$k_1 \times 10^{-3}$
14.4	1.33	12.95	1.41
16.5	1.28	14.32	1.49
17.2	1.42	16.36	1.47
17.2	1.35	17.97	1.56
17.6	1.44	20.12	1.58
19.9	1.42		
21.2	1.47	Av.	1.50±.05
21.6	1.44		
Av.	1.39±.06		

respect to hydrogen. On the assumption of reaction (3b) the first-order constants (k'') are related to the nitrogen dioxide by $k''=k_{3b}[NO_2]$ whence k_{3b} can be obtained using values for nitrogen dioxide given by the equilibrium constant. The results are given in Table I.* The temperature dependence is shown in curve *D* of Fig. 2. The corresponding results for carbon monoxide are shown in curve *B*. The usual procedure yields an energy of activation of 20 kcal. which is considerably less than that for the carbon monoxide reaction.

We can say in general that the hydrogen results confirm the previous interpretations concerning the homogeneous reaction but have not given k_1 values that can be considered as thoroughly established. The interfering reactions have relatively high temperature coefficients so that it ought to be possible to get good results at lower temperatures. With a temperature sufficiently low reactions (3) and (4) will be eliminated. It will be necessary then for reaction (2) to be fast enough so that (5) will not predominate. Both of these would be expected to have low temperature coefficients.

Discussion of the Heterogeneous Reaction

The study of the kinetics of the slow reactions in these systems should lead to a better understanding of the explosive reactions. The various theoretical developments have assigned a chain branching role to nitrogen dioxide to explain the lower explosion limit and a chain breaking function to account for the upper limit. Von Elbe and Lewis[3] assume the branching reactions to be

$$NO_2+X\rightarrow NO_3+OH, \quad (6)$$

$$NO_3+H_2\rightarrow OH. \quad (7)$$

Reaction (7) is opposed to our reaction (2b). Perhaps both are realized. If the former were extensive then it would require that in our k_1 type experiments that the rate be dependent on hydrogen because of the chain that is assumed to arise with the hydroxyl radical. Some experiments at 684°K showed no effect of hydrogen when this was changed from 510 to 340 mm. Also, if (7) were just within our experimental error there is the question as to whether it would then be sufficient to provide the necessary chain branching.

The surface studies indicate a small effect both on the slow reaction and on the reaction in the explosive area. It is very effective in the case of carbon monoxide and as pointed out earlier may be more important for hydrogen than indicated by our present experiments. The similar character of the explosion areas for hydrogen and carbon monoxide indicate a similar mechanism. The work of Calhoun contains a significant result in that when nitrogen dioxide and oxygen stand for various times up to 100 minutes that the rate drops to half the value. This might indicate a competition of two adsorbed substances for the active parts of the surface. If nitric oxide were more strongly adsorbed than oxygen and if it were assumed that the chains are initiated at the walls, then the increase of rate with increase of nitrogen dioxide would continue until the nitric oxide crowded its reaction partner off the wall with a corresponding decrease in rate. Again, in the light of our interpretation of the homogeneous reaction we might say that the centers become covered with NO_3 molecules which serve as chain origins. If the concentration of nitric oxide becomes high then we have reaction (5) with the loss of a chain possibility and a decrease in rate. It would still be necessary to follow von Elbe and Lewis for some homogeneous chain branching process to account for the explosions.[7]

An alternative explanation of our k_1 kinetics on the basis of relative adsorption characteristics would presume a much greater surface effect in this connection than was observed.

* The precision of all rate constants given here is well illustrated by the data of Calhoun and Crist and examples need not be given.

[7] See in this connection R. G. W. Norrish, J. Am. Chem. Soc. **60**, 1513 (1938).

Discussion

R. H. Crist, *Columbia University:* The reactions with hydrogen were disappointing in not providing better data for the k_1 determination. Thus far the primary interest has been to use a third substance that would react with NO_3 rapidly so that the formation of this would be

the rate determining step. It has been necessary to work at a temperature sufficiently high that the NO_2 would be lessened by reaction with CO or by decomposition. (The reaction of CO with NO_2 does not involve a pressure change and hence does not figure in the measured rate.) It was considered possible to work at a temperature below which NO_2 would neither decompose nor react with CO, namely, around 150°C. The reactions would be

$$NO+O_2 \rightarrow NO_3 \quad (1)$$

$$NO_3 \rightarrow NO+O_2 \quad (1a)$$

$$NO_3+NO \rightarrow 2NO_2 \quad (2)$$

$$NO_3+CO \rightarrow NO_2+CO_2. \quad (3)$$

The kinetic analysis is made on the assumption that all reactions are in process. In the first place, the ratio k_2/k_3 can be obtained from the measured rates of these two reactions, i.e.,

$$\frac{R_2}{R_3}=\frac{k_2[NO_3][NO]}{k_3[NO_3][CO]},$$

where R_2 and R_3 are obtained by analysis and the NO and CO from the initial pressures.

To obtain k_1 we write,

$$R_3=k_3[CO][NO_3],$$

whence by the usual treatment of intermediates we obtain

$$\frac{1}{R_3}=\frac{1}{k_1[NO][O_2]}+\frac{k_{1a}+k_2[NO]}{k_1k_3[NO][O_2]}\cdot\frac{1}{[CO]}.$$

Here, with NO and O_2 constant the rate will be determined as a function of CO. The plot of $1/R_3$ against $1/[CO]$ gives k_1 from the intercept. The slope will yield k_{1a}/k_3 since k_1 and k_2/k_3 are now known.

To evaluate k_3 use is made of the oxygen equation

$$-\frac{d[O_2]}{dt}=k_1[NO][O_2]-k_{1a}[NO_3]$$

which on introducing the value for NO_3 as before yields

$$R=\frac{k_1k_2[NO]^2[O_2]+k_1k_3[NO][O_2][CO]}{k_{1a}+k_2[NO]+k_3[CO]}.$$

The first term in the numerator and the first two terms of the denominator will be constant and written as C_1 and C_2, respectively, and the equation takes the form

$$RC_2+(R[CO]-k_1[NO][O_2][CO])k_3-C_1=0.$$

If we have at least three different values of CO and R we can obtain k_3 and from this and the above ratios we can obtain k_2 and k_{1a}.

This determination of the rate constants of (1) and (1a) makes possible the calculation of the termolecular rate constant of Bodenstein for the nitric oxide oxidation.

The experimental problem requires a determination of carbon dioxide and nitrogen dioxide after a change sufficiently small that the initial conditions are not altered appreciably. The experiments indicate that favorable rates will be found around 170°C.

Guenther von Elbe, *Coal Research Laboratory, Carnegie Institute of Technology,* and **Bernard Lewis,** *U. S. Bureau of Mines:* We should like to amplify the statement of Crist and Wertz concerning the relation of the reaction mechanism proposed by us[8] for the explosive range to their mechanism for the range of higher NO_2 concentrations. The issue is not between their reaction

$$NO_3+H_2=NO_2+H_2O \quad (1)$$

and our reaction

$$NO_3+H_2=HNO_2+OH. \quad (2)$$

Since at high NO_2 concentrations chains are suppressed, reaction (2) according to our scheme, should be entirely subordinate in water yields to the reaction

$$NO_3+2H_2=NO+2H_2O. \quad (3)$$

The issue, therefore, concerns reactions (1) and (3).

If reaction (1) is admitted to our scheme the correct kinetic expression cannot be obtained. Reaction (3), however, can replace reaction (1)

[8] Von Elbe and Lewis, J. Am. Chem. Soc. **59**, 2022 (1937).

in Crist and Wertz' mechanism as follows:

(a) $NO_2+H_2=NO+H_2O$

(b) $NO+O_2=NO_3$

(c) $NO_3+NO=2NO_2$

(3) $NO_3+2H_2=NO+2H_2O$

(d) $2NO_2=2NO+O_2$.

Reaction (d) has been added as a plausibility, but it is not essential. For low oxygen and high hydrogen concentrations the rate of regeneration of NO_2 by reaction (c) is negligible and, therefore, NO is the main oxide of nitrogen present in the steady state. Reaction (a) then hardly contributes to water formation. Hence,

$$d(H_2O)/dt=2k_b[NO][O_2]$$

as found experimentally. If the concentration of hydrogen is low and the oxygen high, NO_2 is rapidly regenerated by reaction (c) and it becomes the main oxide of nitrogen present. The principal water-forming reaction is now (a) and the rate is accordingly of the first order with respect to hydrogen as found experimentally.

The above mechanism does not conflict with the mechanism for the explosive range. The latter was developed on the assumption that NO_2 is always the main oxide of nitrogen present. This is justifiable because the initial composition of the mixture changes but slightly during the induction period preceding explosion for which the mechanism applies, due both to the short time interval (of the order of seconds as compared with a reaction time of minutes in Crist and Wertz' experiments) and the low concentration of NO_2.

R. H. Crist, *Columbia University:* The suggestion that the main water producing reaction at high hydrogen and low nitrogen oxide pressures involves two molecules of hydrogen could be confirmed by examination of intermediate pressures. Since our original interest was not in this direction the more complex pressure ranges were avoided

J. A. Christiansen, *Royal Polytechnic Institute, Copenhagen:* How certain are you that the reaction $NO+O_2\rightarrow NO_3$ really occurs? In the case of mixtures of ozone and NO_2 a spectrogram gives definite new lines but it is not known for certain that they are due to NO_3. Is there any evidence for the existence of the intermediate NO_3?

R. H. Crist, *Columbia University:* The first-order relationship is the only proof for the assumed reaction. We find that reaction rate is independent of carbon monoxide pressure from 300 to 600 mm. I think that the NO_2 is removed too rapidly for the equilibrium $2NO+O_2\rightleftharpoons 2NO_2$ to become established. This reaction hypothesis will be confirmed when I can determine the Bodenstein constant. I know of no other proof of the existence of the NO_3 in this system but it has always been considered as a good intermediate.

L. S. Kassel: NO_3 is one of our best intermediates. It comes as near to being a stable compound as any intermediate which is used in kinetics

Bernard Lewis, *U. S. Bureau of Mines:* For the chemical, spectral and kinetic evidence for the existance of the molecule NO_3 the following papers may be cited. Schwarz and Achenbach, Ber. **68**, 343 (1935); *Gmelin's Handb. Anorg. Chemie* (8th ed., 1935); von Elbe and Lewis, J. Am. Chem. Soc. **59**, 2022 (1937); **61**, 1350 (1939); Schumacher, Zeits. f. Anorg. Chemie **233**, 47 (1937); E. J. Jones and O. R. Wulf, J. Chem. Phys. **5**, 873 (1937).